A TREATISE ON HEAT

(Including Kinetic Theory of Gases, Thermodynamics and recent advances in Statistical Thermodynamics)

BY

M. N. SAHA, D.Sc., F.R.S.
Late Palit Professor of Physics, Calcutta University

AND

B. N. SRIVASTAVA, D.Sc., F.N.I.
Professor of General Physics, Indian Association for the
Cultivation of Science, Calcutta

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PREFACE TO THE THIRD EDITION

The Second Edition has been out of stock for a long time causing great inconvenience to the vast majority of our readers and particularly students. We regret very much this inconvenience but the delay in bringing out this new edition has been due to various factors beyond our control—the second world war, the difficult post-war conditions and so forth. We have however taken this opportunity to rearrange the book in a more satisfactory form and have largely rewritten the subject matter and have tried to bring it uptodate.

The plan of the book has been somewhat altered to enable us to give a fuller and more advanced treatment of the various topics. After the first two chapters dealing with Thermometry and Calorimetry more or less in a phenomenological way, the three main methods employed in the theory of heat have been developed *viz.*, the Kinetic Theory method, the method of Thermodynamics and that of Statistical Mechanics in Chaps. III to IX. These methods have been applied in subsequent Chapters (X to XIII) to the derivation of Equation of State, phenomenon of Change of Phase, production of Low Temperature and Thermal Expansion, and in Chaps. XV & XVI to the problems of Radiation and Specific Heat. Thermodynamics of quantum-mechanical systems is dealt with in Chap. XVII while the application of thermodynamics and quantum statistics to Chemical Equilibria is considered in Chap. XVIII. The Appendix contains numerous useful Notes as in the last edition but new Notes have been added on Thermal Diffusion and Low Temperature Physics on account of the importance which these subjects have attained during post-war years.

Though statistical mechanics has been introduced much earlier, care has been taken to see that the study of the subsequent chapters does not become difficult and with this end in view statistical mechanics has been very sparingly employed until Chap. XVII. The student may therefore omit Chap. IX in the first reading. On account of the comprehensive treatment of the various topics it is hoped that the book will be useful to the student, the research worker, the engineer and the physical chemist alike.

The authors take this opportunity of expressing their gratefulness to numerous friends who pointed out the inaccuracies and shortcomings of the previous editions and offered suggestions for improvement. We are very thankful in particular to the late Prof. R. H. Fowler for his valuable suggestions and criticisms. It is earnestly hoped that this cooperation will be continued.

CALCUTTA
JANUARY, 1950. THE AUTHORS

PREFACE TO THE FOURTH EDITION

It is with profound grief that I present this edition. Professor Meghnad Saha, the senior author of this book, died suddenly on 16th February, 1956 during the course of publication of this book. His death has removed the inspiring personality which originated the idea of writing this Treatise and planned and executed it with such perfection. Fortunately, however, the preparation of the present edition was begun in early 1955 and I had fully discussed with him the various lines of improvement as well as the new topics to be included some of which were even written out with his collaboration. The few changes made therefore are almost as he would have wished them to be.

Several portions of the book where notable progress has been made in recent years have been fully revised and brought up-to-date. Chapter XII as well as Note 17 dealing with low temperature physics have been rewritten and considerable new material added. Production of very high temperatures which has gained importance during recent years for purposes of atomic energy has been discussed at some length in Chapter XVIII. A new Note has been added (Note 21) to give the basic principles and methods of the Thermodynamics of Irreversible Processes as it was considered desirable to familiarise the student with this most notable progress in Thermodynamics during the last twenty years. To facilitate quick consultation an explanation of the Symbols and Notation has been given at the end. With these improvements it is confidently hoped that the book will be found more useful by the vast majority of its readers.

CALCUTTA,
MARCH, 1958. B. N. SRIVASTAVA.

PREFACE TO FIRST EDITION (TEXT BOOK OF HEAT)

This book is largely based on the lectures which the senior author had been giving to the Hons. B.Sc. and M.Sc. classes for the past twelve years. It is intended to give a full, up-to-date and concise account of not only the classical parts of Heat, but also such allied subjects as the Kinetic Theory of Matter, Quantum Theory, Statistical Mechanics and Theories of Thermal Ionisation (State of Matter at High Temperatures). The inclusion of the last two chapters has been a deviation from the orthodox practice but is probably justified by their growing importance. Full and copious references to original treatises and papers have been given. It is therefore expected that the book will be helpful not only to the advanced students all over the world preparing for their degree course, but will also be found helpful by the research workers in Physics, Physical Chemistry and Astrophysics as a book of information and references.

In spite of the care taken in the preparation of the book, it is feared that omissions of important results have been many, and the authors will be thankful if these are brought to their notice.

Besides the various authors and publishers to whom we make our grateful acknowledgement on the next page, our best thanks are due to the students of the B.Sc. Hons. class (1931), *viz.*, Messrs. K. K. Bhargava, R. N. Rai, and B. N. Joshi, for preparing the Contents and the Name Index, to Mr. N. C. Chatterjee, M.Sc., of the Banaras Hindu University, for preparing the Subject Index, to Mr. S. C. Deb, Research Scholar, for verifying the calculations in last Chapter XIV, and to Mr. G. R. Toshniwal for help in writing Chapter VIII.

ALLAHABAD
AUGUST, 1931

THE AUTHORS

FOREWORD TO THE TEXT BOOK OF HEAT

The influence of temperature on the physical and chemical behaviour of matter forms a field of study of the highest practical and theoretical interest. In recent years, our knowledge of this subject has vastly increased, and the field of research covers a great range of temperatures, commencing from the lowest possible and extending upwards, apparently without any limit, except that of practical attainment. Recent astrophysical researches—which are by no means in the nature of unsupported speculations—indicate the existence of immensely high temperatures in the interior of stellar masses. The senior author of this book has been the pioneer in that fascinating region of research which deals with the progressive breaking up to the atoms and molecules of matter into their constituent parts at high temperatures. The well-known Saha ionisation formula forms the starting point of much recent astrophysical research. It has also a bearing on the electrical phenomena occurring in flames, electric arcs, and other high-temperature conditions in the laboratory or workshop, and therefore possesses high practical importance.

The familiarity with thermodynamics and its applications to physical and chemical theories which led Professor Saha to these classical researches has also made him a most successful expositor of the subject. His experience in the lecture-room and laboratory, first at Calcutta and later at Allahabad, has helped him to produce with the assistance of the junior author, a book in which freshness and width of outlook are combined with clearness and accuracy in detailed exposition. By undertaking the necessarily laborious task of producing a systematic and up-to-date treatise on the Theory of Heat, Professor Saha has earned a claim to the gratitude of the wide circle of readers—both in and outside of India—who, it is confidently hoped, will study this book and appreciate its merits.

210, BOWBAZAR STREET,
CALCUTTA.
14TH JULY, 1931.

C. V. RAMAN.

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It is a pleasure to acknowledge our grateful thanks to our numerous friends and colleagues who have rendered help in the preparation of the book. In particular our thanks are due for

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Chapter XVIII.—To Dr. S. R. Palit of the Indian Association for Cultivation of Science, for valuable criticisms.

NOTES 15 & 16.—to Prof. D. S. Kothari, Scientific Adviser to the Defence Ministry, Government of India and Dr. R. N. Rai of Delhi University for writing out these notes.

NOTES 17 & 18.—to Dr. S. Datta Mazumdar, Lecturer, Calcutta University for help in writing out these notes.

We further acknowledge our indebtedness to the following authors, publishers and societies for allowing us to reproduce diagrams which have appeared in the works mentioned below. In some cases we have mentioned the particular figures in this book and the corresponding figures in the works from which they are reproduced.

Müller-Pouillets, *Lehrbuch der Physik.*

Henning, *Temperaturmessung.*

Nernst. *Grundlagen des neuen Wärmesatzes.*

Jellinek, *Lehrbuch der physikalischen Chemie.*

Watson, *Practical Physics.*

Ewing, *The Steam Engine and other Heat Engines* (Cambridge University Press.)

Burgess and Le Chatelier, *The Measurement of High Temperatures.*

Philosophical Magazine.

Proceedings of the Physical Society of London.

Astrophysical Journal.

Physical Review.

Bulletin of the Bureau of Standards.

Journal of the American Chemical Society.

Journal de Physique.

Le Radium.

Leiden Communications.

Proceedings of the Koninlijke Akademie der Wettenschappen, Amsterdam.

Proceedings of the Royal Society, London. Chap. II. Figs. 7, 8, 18; Chap. XIV, Fig. 21.

Philosophical Transactions of the Royal Society. Chap. II, Fig. 10; Chap. III, Figs. 2, 3; Chap. XIII, Fig. 15.

Zeitschrift für Physik. Chap. I, Fig. 4; Chap. III, Figs. 11, 25, Chap. XI, Figs. 6, 15; Chap. XV, Fig. 15; Chap. XVI, Figs. 3, 5.

Physikalische Zeitschrift. Chap. II, Fig. 23; Chap. III, Fig. 18.

Annalen der Physik. Chap. II, Figs. 9, 13; Chap. III, Fig. 23; Chap. X, Fig. 8; Chap. XI, Fig. 14; Chap. XIII, Fig. 3; Chap. XVI, Fig. 15.

Handbuch der Physik. Chap. VIII, Fig. 1; Chap. X, Fig. 7; Chap. XII, Fig. 12; Chap. XIV, Fig. 11; Chap. XV, Fig. 30. Reproduced by the kind permission of Messrs. Julius Springer & Co., Berlin.

Handbuch der Experimental-physik. Chap. XI, Figs. 16, 19; Chap. XII, Figs. 7, 15, 17, 29; Chap. XIV, Figs. 3, 14, 17; Chap. XV, Figs. 4, 13, 14, 19, 21, 22, 23.

Ezer Griffiths, *Methods of Measuring Temperature.* Chap. I, Figs. 5, 6, 7; Chap. XV, Figs, 24, 25, 26, 28 from diagrams on pp. 53, 52, 34, 84, 85, 90 and 115 of the book respectively.

Andrade, *Engines.* Chap. IV, Figs. 1, 11, 14, 16; Chap. XII, Fig. 2 respectively from pages 107, 195, 211, 213, 239 of the book by the kind permission of Messrs. G. Bell & Sons, Limited, London.

Partington and Shilling, *Specific Heat of Gases.* Chap. II, Figs. 17, 19, 22, 24, 25 respectively from pages 108, 127, 76, 84, 143 of the book.

Preston, *Theory of Heat.* Chap. II, Figs. 6, 16; Chap. XV, Fig. 27. Reproduced from the said book by the kind permission of Messrs. Macmillan & Co.

THE AUTHORS.

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CHAPTER I

THERMOMETRY

1·1. Concept of Temperature.—The sensation of heat or cold is a matter of daily experience. By the mere sense of touch we can say whether a substance is hotter or colder than ourselves. The hot body is said to possess a higher temperature than the cold one.

But the sense of touch is merely qualitative, while scientific precision requires that every physical quantity should be measurable in numerical terms. Further, the measurements must be accurate and easily reproducible. This requires that the problem should be handled objectively and the sense of touch should be discarded in favour of something which satisfies the above criteria. Let us see how this can be done.

When two bodies are brought in contact or communicate with each other through a wall, it is found that, in general, there is a change in their properties, such as volume, pressure, etc., due to exchange of heat. Finally a state is attained after which there is no further change as long as external conditions do not change. This is called an *equilibrium state* of the combined system. The two bodies are then said to be in *thermal equilibrium* with each other.

Now consider two systems A and B separated from each other by an adiabatic wall, but each is in contact with a third system C through a wall which allows heat to pass (diathermic). Experiments show that when such an arrangement is set up, both A and B reach thermal equilibrium with C with appropriate changes in their properties. Then if the adiabatic wall between A and B is replaced by a diathermic wall, it is found that no further change occurs in A and B showing that A was also in thermal equilibrium with B. These experimental facts may be stated concisely in the following form:

Two systems in thermal equilibrium with a third are in thermal equilibrium with each other.

This law of thermal equilibrium is the basis of the existence of the concept of temperature. In the above example the system C may be taken to be an ordinary mercury thermometer with which the bodies A and B are simultaneously or successively in thermal equilibrium. All these three bodies may be said to possess a property that ensures their being in thermal equilibrium with one another. We call this property ***temperature***. The temperature of a system is a property which determines whether or not a system is in thermal equilibrium with other systems. Evidently this temperature can be measured by observing some such property of any one of these systems which varies with the addition of heat.

Heat causes many changes in the physical properties of matter some of which are well-known, *e.g.*, expansion, change in electrical resistance, production of electromotive force at the junction of two dissimilar metals, etc. All these thermometric properties have been utilised for the measurement of temperature. The earliest and commonest thermometers utilise the property of expansion. Mercury-in-glass is universally employed as a thermometer for ordinary purposes, but though it is simple, convenient to use and direct-reading, it is not sufficiently accurate for high-class scientific work.

For the quantitative measurement of temperature we must select a ***standard temperature interval*** between two easily reproducible fixed temperatures just as we select the standard of length (metre) to be the distance between two fixed marks. The two fixed temperatures selected for this purpose are the melting point of ice and the boiling point of water. The next step is to sub-divide this standard temperature interval into sub-intervals by utilising some thermometric property and call each sub-interval a *degree of temperature.* On the Celsius scale this standard interval is divided into 100 degrees. The third step is to assign some arbitrary value to the temperature of one of these fixed points and reckon all temperatures from that point. On the Celcius scale the lower fixed point is called 0°C. It will be seen that the empirical temperature scale so defined is more or less arbitrary and any number of such scales may be selected. In fact this devise merely serves to register temperature rather than measure it since multiples of temperature can have no meaning with reference to the temperature unit. It is only with absolute temperatures and on the basis of Carnot's principle that it becomes possible to arrive at a measurement of temperatures by the definition of a ratio when the absolute zero of temperature is also fixed.

1·2. Mercury Thermometer.—Everybody is familiar with the ordinary centigrade thermometer. It consists of a glass bulb containing mercury to which a graduated capillary stem is attached. The freezing point of water is marked 0°C. and the boiling point 100°C. and the interval divided into 100 equal parts. This scale was first introduced by Celsius (1742) and is now adopted for all scientific work. Other scales in ordinary use today are those introduced by Fahrenheit (1714) and Réaumur. But Fahrenheit was the first to choose mercury as the thermometric substance on account of its many advantages. It does not wet glass, can be easily obtained pure, remains liquid over a fairly wide range, has a low specific heat and high conductivity; it is opaque and its expansion is approximately uniform and regular. But we must not forget its several drawbacks. The specific gravity and surface tension of mercury are large, and the angle of contact with glass, when mercury is rising, is different from that when it is falling.

The range of an ordinary mercury thermometer is limited by the fact that mercury freezes at −38·87°C. and boils at 356°C. but the upper limit can be raised to about 500°C. by filling the top of the tube with nitrogen under pressure. The thermometric glass must be of special quality: it should be stable and should rapidly return to its normal state after exposure to high temperatures. The glasses generally employed are *verre dur* and Jena 16^{III} for better-class thermometers and borosilicate glass 59^{III} and 1565^{III} for high-temperature work. Thermometers have, however, been constructed of quartz containing mercury under pressure, and these can be used up to 750°C.

Mercury thermometers are generally employed for rough work. If they are at all used for accurate work, various corrections must be applied to get the true temperature. The important ones among them are the following:—

(1) Calibration Correction. This is due to want of uniformity in the bore of the capillary tube.

(2) Correction due to change in the fundamental interval from 100 to $100+\delta$ (say) where δ has any value.

(3) Correction due to shift of the zero. This is very important since glass after exposure to high temperatures returns to its normal state only after a very long time.

(4) Exposed Stem Correction. Part of the stem and hence the contained mercury does not acquire the temperature of the bath.

(5) Correction due to changes in the size of the bulb caused by variable internal and external pressure.

(6) Correction for thermal expansion of the material.

For details concerning the application of these corrections and other useful information see Glazebrook, *A Dictionary of Applied Physics*, Vol. 1 (Article on Thermometry); *Temperature, Its Measurement and Control in Science and Industry* (1941), pp. 228—256 (Article by Busse).

1·3. Special Types of Liquid Thermometers.—The ordinary mercury thermometer is not suitable for certain purposes; for this reason special types of thermometers have been devised. They are modifications of the ordinary thermometer designed to serve the particular end in view.

For *meteorological* purposes thermometers are required to indicate the maximum and minimum temperatures to which they have been exposed during a certain period. Six devised a combined maximum and minimum thermometer which is indicated in Fig. 1. The bulb A and part of the tube is filled with alcohol up to the level B, then with mercury up to C above which again there is alcohol up to D. The glass indexes I, I, have each an iron wire attached (shown separately), and placed above B and C in each tube. When the temperature rises, the alcohol in A expands and the expanding mercury pushes upwards the index above C to its maximum limit. With a fall in temperature this index is undisturbed while the index above B is pulled upwards by the contracting alcohol, but is left behind when the temperature rises. The iron wire attached to the glass index prevents it from falling under its own weight and enables its position to be adjusted from outside.

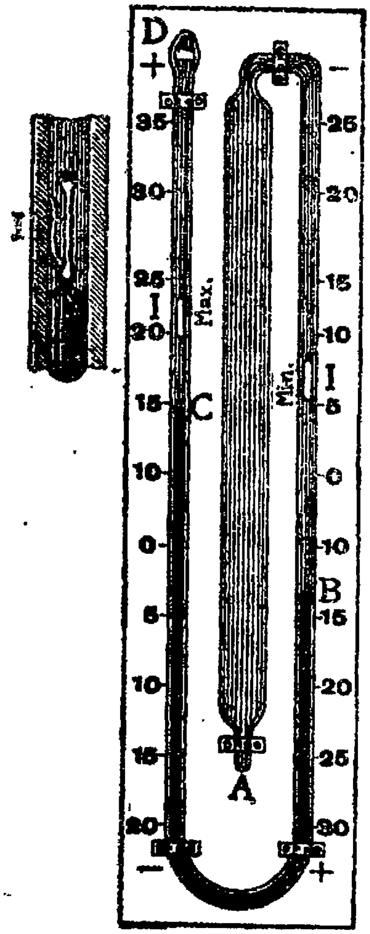


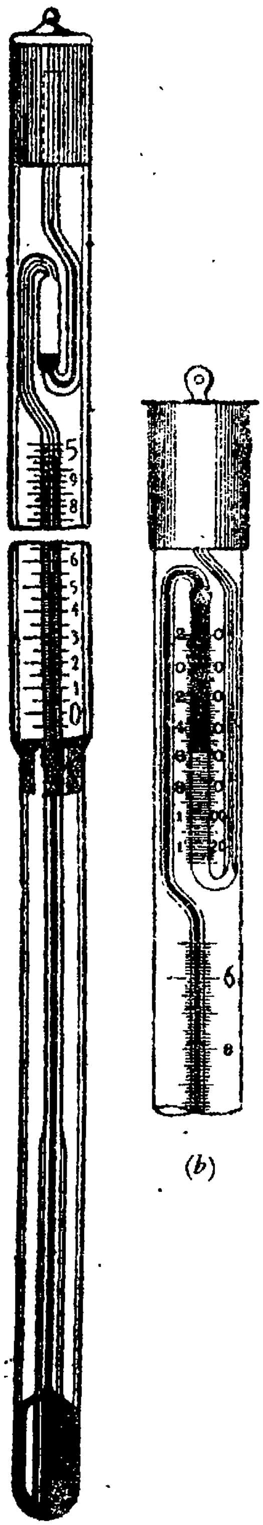
Fig. 1.—Six's maximum and minimum thermometer.

For determining the temperature of the air in meteorology, the Aspiration thermometer has been devised by Assmann. It consists essentially of a sensitive mercury thermometer whose bulb is protected from solar radiation by a double-walled jacket. By means of an aspirator a current of air is kept circulating past the bulb. The bulb thus takes little time to acquire the temperature of the atmosphere.

The clinical thermometers in ordinary use are mercury thermometers of short range of the maximum type. The stem just above the bulb has constriction which the mercury passes when its temperature rises. On cooling, the mercury is unable to force its way back. The range of temperatures is 95°F. to 110°F., and the bulb is very thin and the capillary bore very fine. The mercury thread is rendered easily visible by constructing lens-front thermometers.

For accurate work, such as the determination of the boiling and melting points of organic substances, several short-range thermometers are employed between the range 0 and 450°C. They are called *chemical* thermometers. Benzol and Toluol thermometers are amongst the many that are in use.

The *Beckmann* thermometer, indicated in Fig. 2, is used to measure small changes of temperature with a high degree of accuracy. The stem is here marked from 0 to 5 representing approximately degrees centigrade and every degree is divided into 100 equal parts. There is a reservoir at the top of the instrument (shown separately at *b*) to enable the range to be varied. To set the thermometer to any desired range, the bulb is heated to expel mercury into the reservoir and the instrument gently tapped when the mercury column breaks near the reservoir and some mercury is transferred into it. Next the Beckmann thermometer is immersed along with an auxiliary thermometer in a bath whose temperature is varied till the mercury stands at the 0 division of the former. The temperature corresponding to the zero of the Beckmann thermometer is thus observed on the auxiliary thermometer, and by varying the amount of mercury in the bulb this is adjusted to be near the desired range. The value of each scale division varies with the quantity of mercury in the bulb and a correction curve for different settings of the zero is supplied with the instrument from which the correction at any point of the scale may be obtained. The true value of a scale



(*b*)

(*a*)

Fig. 2.—Beckmann thermometer

division may also be obtained by calculation if the expansion of mercury and glass be known.

1·4. Gas Thermometers.—The fundamental disadvantage of liquid thermometers is that two thermometers containing different liquids, such as mercury and alcohol, and graduated as on page 3, will agree probably only at 0°C. and 100°C. and at no other temperature. This is due to the fact that the expansion of the two liquids is not regular and similar. Thus the mercury thermometer of page 3 would give an arbitrary[1] scale of temperature. Moreover, the corrections to be applied to it (p. 3) are uncertain and known only approximately. Hence for accurate work the mercury thermometers are calibrated (see §1·12) by actual comparison with a resistance thermometer throughout the entire range. Even then the mercury thermometer is rarely used for accurate work, and for all standard work gas thermometers are employed.

Gases possess several advantages as a thermometric substance. Their expansion is large so that gas thermometers will be more sensitive and the expansion of the containing vessel will necessitate only a very small correction. They can be obtained pure and remain gaseous over wide ranges of temperature. Further, the scales furnished by different gases are *nearly* identical since the expansion of all gases is found to be almost perfectly regular. Thus the temperature t given by the relation $t = 100(X_t - X_0)/(X_{100} - X_0)$ where X may stand for the volume or the pressure at the temperature denoted by the subscript, is found to yield nearly identical values whatever gas we may use as the thermometric substance. As will be shown presently, on extrapolation to zero pressure, *i.e.*, to the state of a perfect gas, these scales of temperature become *absolutely* identical. Further, it will be shown that the temperature scale furnished by a perfect gas is absolute and universal; it does not depend upon the properties of any particular

---

[1] The volume v_t of a certain mass of mercury at any temperature t lying between 0 and 100°C. as measured on the perfect gas scale is given by the relation

$$v_t = v_0\,(1 + 1{\cdot}8182.10^{-4}\,t + 0{\cdot}78.10^{-8}\,t^2).$$

Thus the relation is not linear and the readings of the mercury thermometer as calibrated on page 3 will not agree, even after applying the corrections mentioned on page 3, with those of a perfect gas thermometer even in the range 0 – 100°C.

substance. It is for these reasons that gas thermometers are used as primary standards with which all others are compared and calibrated.

The theoretical bases underlying the use of gas as thermometric substance are the laws[1] of Boyle and Charles. Let the gas be initially at pressure p_1, volume v_1 and temperature t_1°C. If we perform the change by first changing the pressure from p_1 to p_2 and next the temperature from t_1 to t_2, we have from these laws,

$$p_1v_1 = p_2v', \quad \frac{v'}{v_2} = \frac{1+at_1}{1+at_2},$$

where v' is the intermediate volume and a the coefficient of expansion at constant pressure. Combining these two equations we have

$$\frac{p_1v_1}{p_2v_2} = \frac{1+at_1}{1+at_2}, \tag{1}$$

which is the gas equation.

Experiments show that the volume coefficient of expansion a is nearly the same for all the permanent gases of nature and is absolutely identical for all of them if their behaviour is extrapolated to the state of zero pressure, *i.e.*, the state of perfect gas. The value of a for a perfect gas from the best recent determinations is 0·0036608. A gas thermometer filled with a gas at vanishingly low pressure will then give the same scale of temperature whatever the gas. This is called the Avogadro scale of temperature or the gas scale.

The temperature $t = -1/a$, *i.e.*, $1/a$ degrees below the ice point is by definition called the *absolute zero*[2] If we measure temperatures from this zero, the ice-point is given by $1/a$, the steam point by $(1/a)+100$, and generally any temperature t°C. by $(1/a)+t =$ T°K. The scale so obtained is called the *Absolute Scale* or *Kelvin Scale* and will be denoted by °K. Hence equation (1) becomes

---

[1] Preliminary experiments show that these laws are obeyed by the so-called permanent gases in nature. More accurate experiments (Chap. X), however, reveal the fact that such gases obey these laws only approximately and not rigorously, and in some cases considerable departures are observed. A *perfect gas* is defined as one which will obey Boyle's law and Joule's law (Chap. II) rigorously.

[2] The absolute zero thus defined is shown from thermodynamic considerations (Chap. VI) to be the lowest temperature possible. Hence the idea of this absolute zero is very important (see further §1·11).

$$\frac{p_2v_2}{p_1v_1}=\frac{(1/a)+t_2}{(1/a)+t_1}=\frac{T_2}{T_1};$$

or

$$\frac{p_2v_2}{T_2}=\frac{p_1v_1}{T_1}=\frac{p_0v_0}{T_0}\text{ (say)}, \quad . \quad . \quad . \quad (2)$$

where the suffix 0 denotes the quantities at 0°C. The quantity p_0v_0/T_0 is known as the gas constant and varies as the mass of the gas taken, but is the same for equivalent gram-molecules of all perfect gases. For one gram-molecule this quantity is usually denoted by R. Hence the equation can be written generally in the form $pV=n^*RT$ where n^* denotes the number of gram-molecules of the gas.

We have already stated that the real gases do not obey the perfect gas laws. How can we then find the value of T_0 and R? The method of doing this will be indicated in section 1·10. There it is shown that for a perfect gas $a = 0\cdot0036608$ per °C. whence $T_0 = 273\cdot16$ degrees and $R = 8\cdot314\times10^7$ ergs per degree.

Equation (2) furnishes two ways of measuring temperature. The pressure may be kept constant and the volume observed at different temperatures giving us the constant pressure thermometer; or the volume may be kept constant and the change in pressure noted, a principle utilised in the constant volume thermometer.

1·5. Standard Gas Thermometers.—The constant-pressure air thermometer has been defended by Callendar on various grounds: (1) the apparatus and the calculations are simple; (2) the internal pressure on the bulb does not increase as the temperature rises; (3) accuracy of the result depends upon the accuracy of weighing. Nevertheless the instrument does not give concordant results and has been replaced by the constant-volume thermometer as a standard. The normal thermometer selected by the Bureau International des Poids et Mesures and everywhere adopted today is the constant-volume hydrogen thermometer filled with gas at a pressure of 1 metre of mercury at the temperature of melting ice. It consists essentially of two parts: the bulb enclosing the invariable gaseous mass and the manometer for measuring the pressure. Fig. 3(*a*) represents the thermometer[1] diagrammatically.

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[1] A high-precision constant-volume gas thermometer has been described by Beattie and co-workers (*Proc. Amer. Acad. Arts and Sciences*, **74**, 327, 1941).

The bulb C is a platinum-iridium tube one litre in capacity, 1 metre in length and 36 mm. in diameter. It is attached to the manometer by a capillary tube of platinum one metre in length. The manometer consists of two tubes A and B, and the stem of the barometer R dips into A. The barometer tube is bent so that the upper surface of mercury in it is exactly above B and these levels can be read off by a cathetometer furnished with three telescopes. The number of observations to be taken is thus reduced to two. B consists of two columns of mercury separated by the steel-piece H and both these columns communicate with A. By raising or lowering the mercury reservoir M, the mercury surface in the lower part of B is just made to touch a fine platinum point P [shown magnified in Fig. 3(*b*)], projecting from the steel-piece H, and thus the volume of the enclosed gas is kept constant.

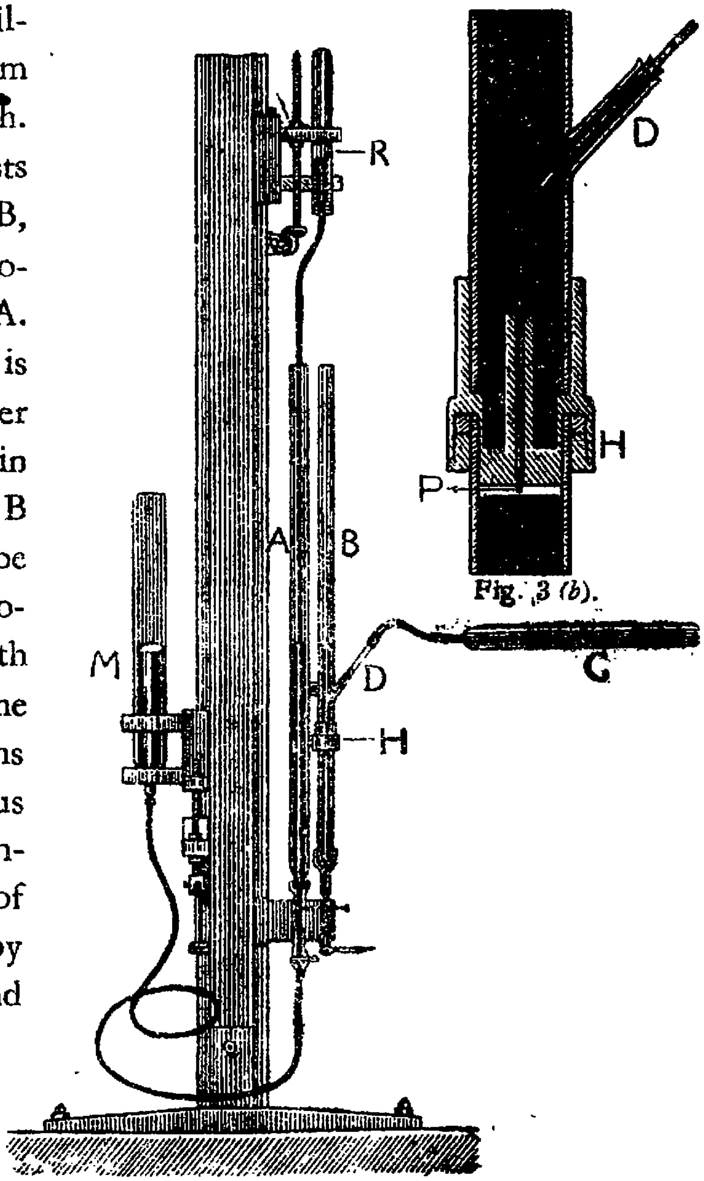

Fig. 3 (*b*).

Fig. 3(*a*).—Constant-volume hydrogen thermometer.

The thermometer described above is suitable for measuring temperatures up to 500°C. For higher temperatures certain modifications are necessary which will be discussed in section 1·25. The range of gas thermometers with proper modifications can be extended from −260°C. to 1600°C.

We shall now deduce a formula for converting the observed pressure readings into corresponding temperatures. If p_0, p_{100}

denote the pressures indicated by the manometer at the ice-point and the steam-point respectively, and T_0 the ice-point on the absolute scale, then

$$\frac{p_{100}}{p_0} = \frac{T_0+100}{T_0},$$

whence

$$\frac{1}{T_0} = \frac{p_{100}-p_0}{100\,p_0} = \beta,$$

where β is the coefficient of expansion at constant volume, and is known when p_0 and p_{100} are determined experimentally. To find the absolute temperature corresponding to any observed pressure p_1, we have

$$\frac{p_1}{p_0} = \frac{T_1}{T_0}; \quad \text{or} \quad T_1 = \frac{p_1}{p_0}\cdot\frac{1}{\beta}, \qquad . \quad . \quad . \quad (3)$$

since $T_0 = 1/\beta$.

ACCURATE GAS THERMOMETRY

1·6. Gas Thermometer Corrections.—In the preceding section the equation was developed on the assumptions (1) that the whole gas attained the temperature to be measured, its volume remaining constant and there being no disturbing factors; and (2) that the gas obeyed the perfect gas laws. Actually, however, none of these assumptions is true and consequently corrections are necessary. First we shall correct for the former.

Here the chief[1] sources of error are the following :—

(*a*) The gas in the 'dead space' is not raised to the temperature of the bulb. The 'dead space' consists of the space inside the capillary tube and in the manometer between the mercury level and the steel-piece H. Its initial and final temperatures are also different.

(*b*) Increase in the volume of the bulb C with rise of temperature.

(*c*) Change in volume of the bulb due to changes in internal pressure.

(*d*) Change in density of mercury on account of temperature changes.

Let V_0 denote the volume of the bulb and H_0 the pressure of the contained gas at 0°C. If the volume of the dead space be v and its temperature throughout the experiment be t while α denotes the volume coefficient of expansion of the enclosed gas, then the volume of the whole gas at N.T.P. will be

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[1] There are about 25 corrections in all and the task of correcting for all of them is extremely tedious and laborious. For the method of applying these corrections Guillaume's *Thermométrie de Précision* may be consulted.

$$\left(V_0+\frac{v}{1+\alpha t}\right)\frac{H_0}{760}.$$

When the bulb is heated to θ°C. and the pressure becomes H_0+h, the same volume is given by

$$\left\{\frac{V_0(1+\gamma\theta)+bh}{1+\alpha\theta}+\frac{v}{1+\alpha t}\right\}\frac{H_0+h}{760},$$

where γ is the coefficient of volume expansion of the bulb and b the coefficient of internal pressure. bh denotes the increase in the volume of the bulb due to the increase in internal pressure by h. Equating the above two expressions we get

$$V_0H_0=\frac{\{V_0(1+\gamma\theta)+bh\}(H_0+h)}{1+\alpha\theta}+\frac{vh}{1+\alpha t}$$

whence

$$\alpha\theta=\frac{H_0+h}{H_0}\cdot\frac{V_0(1+\gamma\theta)+bh}{V_0}+\frac{hv}{H_0V_0}\cdot\frac{1+\alpha\theta}{1+\alpha t}-1. \quad . \quad . \quad (4)$$

Since θ, the temperature to be determined, occurs on the right, the uncorrected value of θ, *viz.*, $\theta=h/H_0\alpha$ is substituted there to give a more accurate value of θ. This value may be again substituted on the right to give a still more accurate value of θ. The process can be repeated indefinitely. This is called the *method of successive approximations* and is very commonly employed in Physics. Generally the process need be performed only once or twice as the result then obtained attains the accuracy permitted by the observations themselves.

1·7. Perfect Gas Scale.—We shall now correct for the second assumption, *viz.*, for the departure of gases from Boyle's law. In order to do this we must know the actual equation of state (Chap. X) of the substance.

We shall denote by t_v and t_p the temperatures as actually recorded on a constant volume and a constant pressure thermometer containing a real gas, while t will denote the corresponding reading given by a perfect gas thermometer. Then from definition

$$t_v=\frac{p_t-p_0}{p_{100}-p_0}\times 100, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$t_p=\frac{v_t-v_0}{v_{100}-v_0}\times 100. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If the quantity of gas is the same in both the thermometers (*i.e.*, at 0°C. the pressure and volume in both is p_0, v_0), then if the gas obeys Boyle's law we have

$$v_0p_t=(pv)_t=v_tp_0. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Thus multiplying (5) by v_0 and making use of (7) we get

$$t_v = \frac{(pv)_t-(pv)_0}{(pv)_{100}-(pv)_0} \times 100,$$

and multiplying (6) by p_0 and using (7),

$$t_p = \frac{(pv)_t-(pv)_0}{(pv)_{100}-(pv)_0} \times 100.$$

Thus for a gas which obeys Boyle's law the temperatures read on a constant pressure and on a constant volume thermometer are identical, and each is given by

$$t = \frac{(pv)_t-(pv)_0}{(pv)_{100}-(pv)_0} \times 100. \qquad . \quad . \quad . \quad (8)$$

We shall now consider the equations of state of a real gas. As will be clear from a study of Chapter X, the number of such equations deduced from theoretical considerations is very large, nevertheless none of them shows a complete agreement with the experimentally observed facts. Under the circumstances the most satisfactory procedure is to write down the equation of state for every gas from the observed experimental data as far as they are available. As this procedure involves a knowledge and measurement of the temperature, the equation is usually expressed in the form

$$pv = A+Bp+Cp^2+Dp^3+ \ldots, \qquad . \quad . \quad . \quad (9)$$

which was first suggested by Kamerlingh Onnes[1]. The constants A, B, C, D . . . . . are complicated functions of temperature but are independent of the pressure, and are found by performing the compression experiments on the actual gas, *i.e.*, by noting the volume at different pressures (Chap. X) and substituting in equation (9). For our present purpose we are concerned only with the numerical values of these constants at certain fixed temperatures and not with their dependence on the temperature which would require a measurement of the temperature. Holborn and Otto[2] have carried out very careful experiments on a number of gases between the range −183°C. to +400°C. and have given the values of the constants A, B, C. . . . at different temperatures. For oxygen at 0°C. they find that

$$pv = 1{\cdot}00130 - 1{\cdot}30143\times10^{-3}p + 3{\cdot}6898\times10^{-6}p^2\ldots, \qquad . \quad (9a)$$

where p is in metres of mercury and $v=1$ when $p=1$. Thus the constants A, B, C . . . are in rapidly decreasing order of magnitude. The D term is generally negligible and at the pressures employed in gas thermometer C is also negligible. Thus the equation simplifies to $pv = A+Bp$.

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[1] *Leiden Commun.*, No. **71**, 1901.

[2] *Zeits. f. Physik*, **33**, 9, 1925.

From this form of the equation, it is easily seen that at infinitely low pressures ($p \to 0$) the gas obeys Boyle's law ($pv = A$) and would thus behave like a perfect gas. From theoretical considerations given in Chapter X, the same conclusion follows. Hence in order to obtain the readings corresponding to a perfect gas we make observations on a real gas and extrapolate the readings to infinitely low pressure. This method was originally given by Berthelot but he used for this purpose his own equation of state and extrapolated graphically and also algebraically to the state of zero pressure. Using Kamerlingh Onnes' form of the equation the extrapolation becomes very easy and is illustrated below :—

Using the *constant-volume thermometer* let us find any temperature t, say, the boiling point of sulphur. The temperature, as observed on this thermometer is, from definition, given by

$$t_v = \frac{p_t - p_0}{p_{100} - p_0} \times 100.$$

We then perform the compression experiments on the same gas at the two fixed points 0°, 100° and at t°C. (the temperature to be determined). We have then

$$\left.\begin{aligned} p_0\, v_0 &= A_0 + B_0 p_0, \\ p_{100} v_0 &= A_{100} + B_{100} p_{100}, \\ p_t\, v_0 &= A_t + B_t p_t, \end{aligned}\right\} \quad . \quad . \quad (10)$$

where v_0 is the constant volume and the constants A_0, B_0, A_{100}, B_{100}, A_t, B_t, are obtained from the results of the compression experiments. Then from definition

$$\begin{aligned} t_v &= \frac{p_t - p_0}{p_{100} - p_0} \times 100 = \frac{v_0 p_t - v_0 p_0}{v_0 p_{100} - v_0 p_0} \times 100 \\ &= \frac{(A_t - A_0) + (B_t p_t - B_0 p_0)}{(A_{100} - A_0) + (B_{100}\, p_{100} - B_0 p_0)} \times 100 \quad . \quad . \quad \text{from (10)} \\ &= \frac{A_t - A_0}{A_{100} - A_0} \,.\, 100 \left[\frac{1 + (B_t p_t - B_0 p_0)/(A_t - A_0)}{1 + (B_{100} p_{100} - B_0 p_0)/(A_{100} - A_0)}\right] \\ &= t_{lim}\left[1 + \frac{B_t p_t - B_0 p_0}{A_t - A_0} - \frac{B_{100} p_{100} - B_0 p_0}{A_{100} - A_0}\right], \end{aligned}$$

with the help of the binomial theorem and by neglecting quantities of the order $(Bp_0/A)^2$. We have put $(A_t - A_0)100/(A_{100} - A_0) = t_{lim}$ the temperature that would be given by the same thermometer if the initial pressure was infinitely low ($p_0 \to 0$). Hence

$$t_{lim} - t_v = t_{lim}\left[\frac{B_{100} p_{100} - B_0 p_0}{A_{100} - A_0} - \frac{B_t p_t - B_0 p_0}{A_t - A_0}\right] \quad . \quad . \quad . \quad (11)$$

This is the correction to be applied to the reading t_v of the constant-volume thermometer in order to reduce it to the temperature t_{lim} which would be given by the same thermometer if the pressure were infinitely small. All the quantities on the right-hand side except t_{lim} are known. We thus see that t_{lim}, the temperature to be determined, occurs in the correction term. Since, however, the value of the correction is small, we can substitute t_v for t_{lim} on the right and employ the method of successive approximations as already explained.

To find the magnitude of the corrections at any other temperature, the value of the correction at a large number of temperatures is found and then an interpolation curve drawn from which the correction at any temperature can be read.

Constant-pressure thermometer.—The temperature t_p recorded by this thermometer is, from definition, given by (6). Multiplying by the constant pressure p_0 we have

$$t_p = \frac{p_0 v_t - p_0 v_0}{p_0 v_{100} - p_0 v_0} \times 100,$$

and making use of (9) as before, we get

$$\begin{aligned} t_p &= \frac{(A_t - A_0) + p_0(B_t - B_0)}{(A_{100} - A_0) + p_0(B_{100} - B_0)} \times 100, \\ &= 100\,\frac{A_t - A_0}{A_{100} - A_0}\left[1 + p_0\frac{B_t - B_0}{A_t - A_0} - p_0\,\frac{B_{100} - B_0}{A_{100} - A_0}\right] \\ t_{lim} - t_p &= t_{lim}\,p_0\left[\frac{B_{100} - B_0}{A_{100} - A_0} - \frac{B_t - B_0}{A_t - A_0}\right]. \quad . \quad . \quad . \quad (12) \end{aligned}$$

which gives the required correction. We can draw an interpolation curve as in the previous case.

It will be seen that the value of t_{lim} is the same whether we use a constant volume or constant pressure gas thermometer and is given by $100\,(A_t - A_0)/(A_{100} - A_0)$. We can, therefore, define the perfect gas scale (Celsius scale) thus :

$$t = 100\,\frac{\underset{p\to 0}{Lim}\,(pv)_t - \underset{p\to 0}{Lim}\,(pv)_0}{\underset{p\to 0}{Lim}\,(pv)_{100} - \underset{p\to 0}{Lim}\,(pv)_0}, \quad . \quad . \quad . \quad . \quad (13)$$

Equations (11) and (12) enable us to obtain the corrections for the temperature range −183 to + 400°C. for which the compression experiments have been performed by Holborn and Otto and consequently the necessary data are available. Above these temperatures due to lack of experimental data this method is inapplicable and a theoretical equation of state must be employed—a method which was used for all temperatures prior to Holborn and Otto's experiments. Above 450°C., however, the correction itself is smaller than the errors of gas thermometry (Sec. 1·6) and is, therefore, generally neglected.

A very good method of obtaining the correction to be applied to the real gas scale is to perform the Joule-Thomson experiment (Chap. XII). The principle underlying this correction will be explained later. Unfortunately, however, the existing data on Joule-Thomson effect are not sufficiently copious to enable us to apply this method and the method given above is almost universally employed.

1·8. We give below (Table 1) the corrections which have to be applied to an actual gas scale in order to convert it to the perfect gas scale. Values of $t-t_p$ and $t-t_v$ are given in the table. The

Table 1.—*Gas Scale Corrections.*

Temperature °C.	Constant pressure			Constant volume		
	Helium	Hydrogen	Nitrogen	Helium	Hydrogen	Nitrogen
−260	..	..	..	+0·041	..	..
−240	..	..	..	+0·033	+0·117	..
−220	..	..	..	+0·026	+0·089	..
−200	..	..	..	+0·020	+0·069	..
−180	..	..	..	+0·015	+0·054	..
−183	+0·029	+0·265	..	+0·019	+0·039	..
−150	+0·015	+0·138	..	+0·014	+0·027	..
−100	+0·005	+0·053	+0·399	+0·008	+0·015	+0·052
− 50	+0·002	+0·016	+0·112	+0·003	+0·003	+0·015
− 25	+0·001	+0·007	+0·039	+0·001	+0·002	+0·006
0						
+ 25	0·000	−0·003	−0·020	−0·001	−0·001	−0·003
50	0·000	−0·003	−0·025	−0·001	−0·002	−0·004
75	0·000	−0·002	−0·018	−0·001	−0·001	+0·003
125	0·000	+0·003	+0·025	+0·001	+0·003	+0·005
150	+0·001	+0·008	+0·056	+0·003	+0·007	+0·011
175	+0·002	+0·013	+0·090	+0·005	+0·011	+0·018
200	+0·002	+0·020	+0·132	+0·008	+0·017	+0·027
225	+0·003	+0·027	+0·178	+0·011	+0·024	+0·038
250	+0·004	+0·035	+0·225	+0·015	+0·032	+0·050
275	+0·005	..	+0·274	+0·019	..	+0·063
300	+0·006	..	+0·320	+0·023	..	+0·080
350	+0·008	..	+0·430	+0·034	..	+0·110
400	+0·010	..	+0·550	+0·046	..	+0·150
450	+0·012	..	+0·670	+0·061	..	+0·190

pressure of the gas at 0°C. is 1 metre of mercury. The corrections for temperatures between $-260°$ and $-180°$C. are given by Onnes and Cath,[1] and those between $-183°$ and $+450°$C. by Holborn and Otto.[2]

A glance at the table shows that the corrections are smallest for helium and largest for nitrogen and except for helium they are less at constant volume than at constant pressure.[3]

1·9. Comparison of Different Gas Scales.—It will be now shown that the scales so furnished by the different gases, when reduced to zero pressure, coincide. Let us calculate the value of the quantity $(A_t-A_0)/A_0t$ for the different gases for various values of t. The necessary data are given by Holborn and Otto[4] who measured these temperatures with a platinum thermometer, which was standardised by comparison with a helium thermometer throughout the range, and thus essentially gave the helium scale. The values of $(A_t-A_0)100/A_0t_{(hel\cdot)}$ so obtained are given in table 2, and are seen to be quite constant and equal to 0·36604 for all gases. Putting $(A_t-A_0)/A_0t_{(hel\cdot)} = a$ and making use of this experimental result we can write for any other gas

Table 2.—*Values of* $100\,\dfrac{A_t-A_0}{A_0\,t_{(hel\cdot)}}$

Gas	Value of 100 $(A_t-A_0)/A_0\,t_{(hel\cdot)}$.					
	$-183°$	$-100°$	$-50°$	100°	200°	400°C.
Helium ..	0·36605	0·36604	0·36602	..	0·36605	0·36604
Hydrogen	0·36604	0·36604	0·36604	..	0·36604	..
Nitrogen ..	..	0·36604	0·36604	0·36603	0·36604	0·36604
Neon ..	0·36604	0·36604	0·36603	0·36604	0·36605	0·36604
Argon ..	..	0·36604	0·36604	..	..	0·36604

$$A_t = A_0\,(1+at_{(hel\cdot)}), \qquad (14)$$

or

$$\mathop{Lim}\limits_{p\to 0}\,(pv)_t = \mathop{Lim}\limits_{p\to 0}\,(pv)_0\,(1+at_{(hel\cdot)}) \qquad (15)$$

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[1] *Leiden Commun.*, No. **156** (a), 1922.

[2] *Zeits. f. Physik*, **33**, 10, 1925.

[3] For corrections according to various other authors see *Temperature, Its Measurement and Control in Science and Industry* (1941), pp. 56-57.

[4] *Zeits. f. Physik*, **23**, 77, 1924; **33**, 25, 1925.

The temperature t_g given by this gas thermometer after reduction to infinitely low pressure is given by

$$t_g = \frac{\lim\limits_{p\to 0}(pv)_t - \lim\limits_{p\to 0}(pv)_0}{\lim\limits_{p\to 0}(pv)_{100} - \lim\limits_{p\to 0}(pv)_0} \times 100 = t_{(thel\cdot)} \qquad . \quad . \ (16)$$

from (15). Thus the temperatures given by all these gas thermometers after reduction to infinitely low pressure coincide, and since at these low pressures Boyle's law is obeyed by all gases, the scales furnished by the constant-pressure and constant-volume thermometer containing any gas, after reduction to infinitely low pressure, must be identical. This is the perfect gas scale and may be attained with the help of any gas thermometer.

1·10. Magnitude of the Coefficient of Expansion and the Gas Constant.

—From Table 2 it is seen that the coefficient of expansion $a = (A_t - A_0)/A_0 t$ is, within limits of experimental error, the same for all gases. From equation (15) it follows that for a gas at infinitely small pressures, the coefficient of volume expansion at constant pressure is the same for all gases. This is called *Charles' law* and is seen here to hold for a gas at infinitely low pressures. The numerical value of a, corresponding to a perfect gas is seen from table 2 to be 0·0036604.

There is one more way of calculating a which was usually employed before this work of Holborn and Otto. The values of α and β, the volume and pressure coefficients as defined in § 1·4 and 1·5 are obtained for different gases at different initial pressures of the gas, and then graphically extrapolated to zero pressure. This was done by Henning and Heuse,[1] and their extrapolation is shown in Fig. 4. It will be seen that the lines for α and β for the different gases intersect at the ordinate corresponding to zero pressure very nearly in a single point, whose magnitude is 0·0036604. Taking into account all

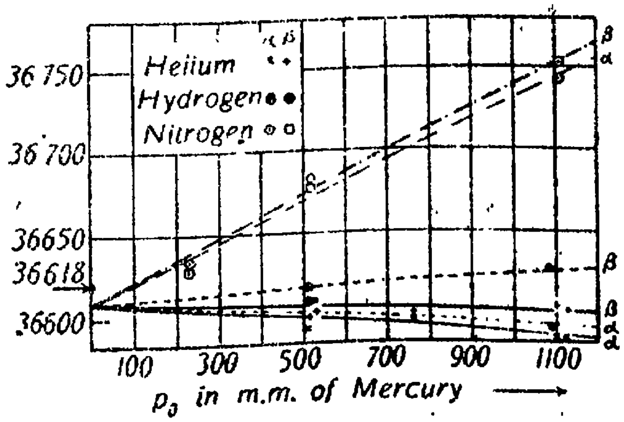

Fig. 4.—Extrapolation of α and β to zero pressure.

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[1] *Zeits. f. Physik*, 5, 285, 1921.

the existing data from different methods obtained in the different laboratories of the world Beattie[1] gives the mean value

$$a \doteq (36608 \pm 2) \times 10^{-7}\ {}^{\circ}\mathrm{C.}^{-1}$$

The perfect gas equation may therefore be written

$$\lim_{p \to 0} (pv)_t = \lim_{p \to 0} (pv)_0 \, (1 + at),$$

and putting $t + (1/a) = T$, where T is the temperature on the absolute scale, we get

$$\lim_{p \to 0} (pv)_t = \lim_{p \to 0} (pv)_0 \, aT. \quad . \quad . \quad . \quad . \quad (17)$$

From Avogadro's law it follows that if we consider a gram-molecule of different gases, the quantity $\lim_{p \to 0} (pV)_0$ will be the same for all gases. Then the above equation can be written in the form

$$\lim_{p \to 0} (pV) = \mathrm{R}T, \quad . \quad . \quad . \quad . \quad (18)$$

where $\lim_{p \to 0} (pV)_0 \, a$ has been put equal to R, a universal constant called the *gas constant.* This is the perfect gas equation. From this as in section 1·5, we deduce $T_0 = 1/a \doteq 273{\cdot}16 \pm 0{\cdot}01^{\circ}\mathrm{K}$. From some accurate experimental data on oxygen Henning[2] obtained $\lim_{p \to 0} (pV)_0 = 22{\cdot}414$ litre×atmospheres. Hence

$$\begin{aligned} \mathrm{R} &= \lim (pV)_0 \, a \\ &= 22{\cdot}414 \times {\cdot}0036608 \times 10^{3} \times 76 \times 13{\cdot}5955 \times 981 \text{ ergs/degree} \\ &= 8{\cdot}314 \times 10^{7} \text{ ergs per degree.} \end{aligned}$$

Since 1 calorie[3] = $4{\cdot}185 \times 10^{7}$ ergs (Chap. III) hence $R = 1{\cdot}987$ calories per degree.

1·11. Thermodynamic Scale of Temperatures.—It will be seen that the absolute temperature has been defined from the relation $T = t + (1/a)$, *i.e.*, in terms of the Celsius temperature as read on the perfect gas scale. Thus the absolute temperature depends upon the property of gases in general, though not upon the particular property of any individual gas. It will therefore be preferable to have a scale which is not dependent even upon the properties of gases. We shall now show how such a scale has been devised.

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[1] *Temperature, Its Measurement and Control in Science and Industry* (1941), p. 87.

[2] *Zeits. f. Physik*, **6**, 69, 1921.

[3] The values of these constants have been taken from Birge, *Rev. Mod. Phys.*, **13**, 236, 1941.

In Chapter VI it will be shown how from Carnot's theorem regarding the performance of ideal heat engines, Lord Kelvin developed a scale of temperature which is *independent of the property of any particular substance*. This is the standard scale of temperature and is known as the *thermodynamic scale*. Further, it is shown there that this scale is quite identical with the perfect gas scale. We thus see that the perfect gas scale which was hitherto shown to depend on the properties of gases now becomes independent of the properties of any particular substance. It is called the thermodynamic scale and is the standard scale adopted in scientific work.

So far we have defined the absolute zero as a temperature $-1/a$ °C. below the ice-point. This definition is hardly satisfactory as no property of the absolute zero has been utilised in defining it and the value of a is known only to a limited degree of accuracy. We shall see later how a satisfactory definition of the absolute zero has been obtained from thermodynamic considerations of engines. On account of the uncertainty in the value of a it is evident that temperatures on the absolute scale are not known so accurately as temperatures on the Celsius scale. For example, the boiling point of oxygen is $-182 \cdot 983$°C. $= 273 \cdot 16 - 182 \cdot 983 = 90 \cdot 18$°K and we are not justified in writing the third decimal place in the last term.

1·12. Standardisation of Secondary Thermometers.—Gas thermometers are very cumbersome to use and require several corrections. Hence in laboratories they are replaced by secondary standards such as the resistance thermometer, the thermo-couple, etc., which have been carefully standardised by comparison with a standard gas thermometer in standardising laboratories, like the National Physical Laboratory in England, Bureau des Poid et Mesures in France, the Physikalisch-Chemische Reichsanstalt in Germany or the Bureau of Standards in Washington.

For this purpose different standard baths may be constructed, each suitable for a particular range. Between 0° and 100°C. a water bath, between 80° and 250°C. an oil bath, between 250° and 600°C., a mixture of potassium nitrate and sodium nitrite and above that an electrical heater is generally employed. For temperatures below 0°C., acetone cooled with solid carbon dioxide can be used down to about —80°C. For still lower temperatures baths containing liquefied gases, such as methyl chloride, ethylene, methane, oxygen, nitrogen and hydrogen boiling under reduced pressure may be employed. For their ranges see Chapter XII.

The secondary thermometers may also be standardised by means of a series of easily reproducible fixed points whose temperatures have been accurately determined. A table of standard temperatures is given in Table 3. The values given in this table are generally those adopted by the Seventh General Conference of Weights and Measures[2] representing thirty-one nations which was

Table 3.—Standard Temperatures for Thermometry.[1]

Temperature°C	Substance	Temperature °C.	Substance
—252·780	B.P. of Hydrogen	419·5	F.P. of Zinc.
—195·81	B.P. of Nitrogen	444·600	B.P. of Sulphur
—182·97	B.P. of Oxygen	630·5	F.P. of Antimony
— 78·5	Sublimation of CO_2	660·1	F.P. of Aluminium
— 38·87	F.P. of Mercury	960·8	M.P. of Silver
0·00	M.P. of Ice	1063	M.P. of Gold
+ 32·38	Transition temperature of $Na_2SO_4 . 10H_2O$	1083	F.P. of Copper
100·000	B.P. of Water	1552	F.P. of Palladium
218·0	B.P. of Naphthalene	1769	F.P. of Platinum
231·9	F.P. of Tin	1960	F.P. of Rhodium
305·9	B.P. of Benzophenone	2443	F.P. of Iridium
320·9	F.P. of Cadmium	2620	M.P. of Molybdenum
327·3	F.P. of Lead	3380	M.P. of Tungsten
		3500 ± 50	M.P. of Carbon

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[1] For a discussion of the sources for these values in addition to Conference Reports see *Handbuch der Physik*, Vol. IX, pp. 591-602 ; *Reports on Progress in Physics*, **6**, 298, 1940. See also Hoge's paper in *Temperature, Its Measurement and Control in Science and Industry* (1941) pp. 141-156 for a critical discussion of the low temperature values.

[2] See a Report by Burgess, *Bull. Bur. Stand.*, **22**, 635, 1928. See also Heuse and Otto, *Ann. d. Physik*, **9**, 486, 1931.

held in October 1927, but some amendments made by the Ninth General Conference[1] in 1948 have also been incorporated.

1·13. Fixed Temperature Baths.—It is frequently convenient to calibrate the secondary thermometers by means of the fixed-point scale given above. The ice-point may be most conveniently obtained by dipping the thermometer in pure melting ice contained in a Dewar flask. This is a double-walled glass or metal vessel whose inner sides are silvered and the space between the walls is evacuated[2]. For the steam-point the hypsometer indicated in Fig. 5 is employed. The diagram explains itself. C is the condenser employed to prevent the water from being lost by evaporation, M is the manometer and T the thermometer. The path of steam is indicated by the arrows. The boiling point of water at the pressure p (in mm. of mercury) is found to be given by the relation

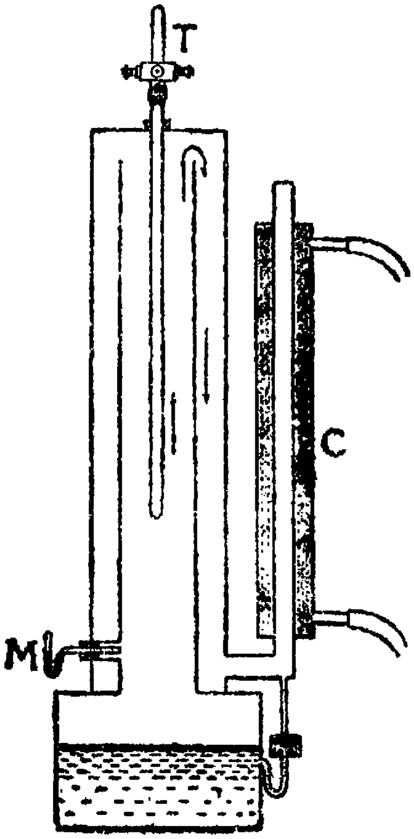

Fig. 5.—Hypsometer.

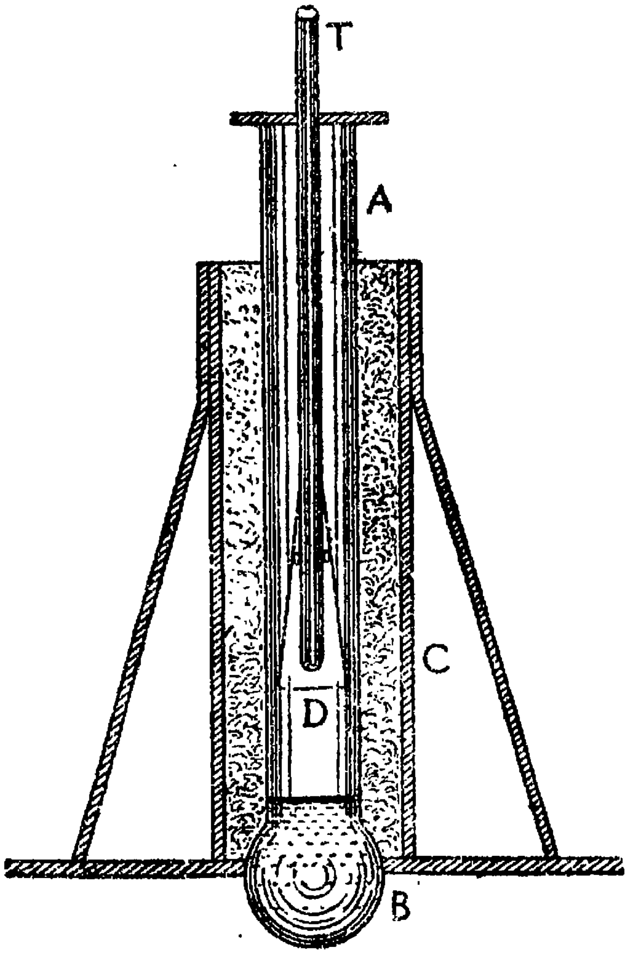

Fig. 6.— Sulphur boiling apparatus.

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[1] See "The International Temperature Scale of 1948," National Physical Laboratory, Teddington (1949); Stimson, *Journ. Res. Bur. Stand.*, Washington, **42**, 209, 1949.

[2] For a complete description see Chapter XII.

$$t = 100{\cdot}00 + 28{\cdot}012\left(\frac{p}{p_0} - 1\right) - 11{\cdot}64\left(\frac{p}{p_0} - 1\right)^2 + 7{\cdot}1\left(\frac{p}{p_0} - 1\right)^3,$$

where p_0 stands for one standard atmosphere. For other fixed points a number of vapour baths in which sulphur, naphthalene, aniline, etc., are used, serves the purpose.

The sulphur boiling-point apparatus has undergone improvement at the hands of several workers[1]. Callendar and Griffiths found that the standard Meyer-tube apparatus was well adapted for the work. It consists of a hard glass cylinder A of diameter 5 cm. and length about 25 cm. to which a spherical bulb B is attached at the bottom (Fig. 6, p. 21). The whole is surrounded by an asbestos chamber C. The thermometer T is fitted with an asbestos or aluminium cone D. This cone serves in two ways: (1) it prevents the condensed sulphur from running down over the bulb and cooling it below the temperature of sulphur vapour; (2) it prevents the bulb from directly radiating to the cooler parts of the tube. Sulphur is placed in the bulb and heated over a flame. A side-tube may be provided in the upper part of the chamber which serves to condense sulphur vapour. The boiling point of sulphur is given by the formula

$$t = 444{\cdot}60 + 69{\cdot}010\left(\frac{p}{p_0} - 1\right) - 27{\cdot}48\left(\frac{p}{p_0} - 1\right)^2 + 19{\cdot}14\left(\frac{p}{p_0} - 1\right)^3,$$

where p_0 stands for one standard atmosphere and p the pressure in mm. of mercury.

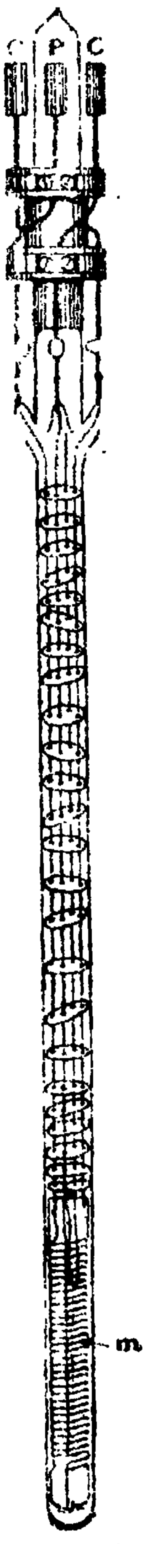

Fig. 7.—Platinum Thermometer.

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[1] For a critical account of the subject Mueller's paper in *Temperature, Its Measurement and Control in Science and Industry* (1941) may be consulted.

Baths for naphthalene and aniline may be constructed by slightly modifying the apparatus of Fig. 5.

RESISTANCE THERMOMETRY

1·14. Platinum Thermometer.—The necessity of secondary standards has been clearly indicated above. Two types of such instruments based on two electrical properties of matter will be described in this chapter. The properties are : (1) variation of electrical resistance of metals with temperature ; (2) variation of thermal electromotive force with temperature. First let us consider the former.

Sir William Siemens was the first to construct in 1871 thermometers based on this principle but the constructional details were unsatisfactory. Later improvements by Callendar and Griffiths have given the instrument its modern form. Figure 7 (p. 22) represents a hermetically-sealed thermometer designed by E. H. Griffiths for laboratory work of high precision. Pure platinum wire free from silicon, carbon, tin and other impurities is selected. It is doubled on itself to avoid induction effects and then wound on a thin plate of insulating mica m. The ends of this wire are attached to platinum leads which pass through holes in mica sheets closely fitting the upper part of the tube, and the other ends of these leads are joined to terminals P, P at the top of the instrument. The mica sheets give the best insulation and prevent convection currents of air up and down the tube. The tube is sealed at the top for, otherwise, moisture would deposit on the mica and break down the insulation. To compensate for the resistance of the leads, an exactly similar pair of leads, with their lower ends joined together is placed close to the platinum thermometer leads, and is connected to terminals marked C, C on the instrument. These are called compensating leads and are joined in the third arm of the Wheatstone bridge as shown in Fig. 9 (p. 26). Then since the ratio arms are kept equal and the compensating and platinum leads have equal resistance at all temperatures, it is the resistance of the platinum coil alone which is determined. For rough work up to 500°C. copper leads may be used and the whole may be enclosed in a tube of hard glass.

But for accurate work platinum leads must be used and the whole must be enclosed in a tube of glazed porcelain.

The precision and reliability of modern resistance thermometers are entirely due to the work of Callendar[1] and Griffiths. They determined the resistance of pure platinum from 0° to 500°C. and found that it was very accurately given by a parabolic formula of the type

$$R_t = R_0(1+\alpha t+\beta t^2), \quad . \quad . \quad . \quad (19)$$

where R_t, R_0 are the resistances at t°C. and 0°C. and α, β are constants. For pure platinum $\alpha = 3\cdot 94.10^{-3}$, $\beta = -5\cdot 8.10^{-7}$.

But Callendar further showed that it was unnecessary to solve this quadratic equation to find t from the value of R_t. He gave a special form to this relation and introduced a nomenclature which has come into general use. Thus we assume the simple relation[2]

$$R_t = R_0\,(1+ct_{pt}), \quad . \quad . \quad . \quad . \quad (20)$$

where c is the mean temperature coefficient of resistance between 0° and 100°C., and define the platinum temperature t_{pt}, which is nearly equal to the true temperature t, by the relation

$$t_{pt} = \frac{R_t - R_{0t}}{R_{100} - R_0} \times 100, \quad . \quad . \quad . \quad . \quad (21)$$

where R_t, R_0, R_{100} respectively denote the resistances at t°, 0° and 100°C. The quantity $R_{100}-R_0$ is called the fundamental interval (F. I.) of the thermometer. Callendar further showed that the difference between the true temperature t and the platinum temperature t_{pt} was accurately given by the parabolic formula

$$t - t_{pt} = \delta\left\{\left(\frac{t}{100}\right)^2 - \frac{t}{100}\right\}, \quad . \quad . \quad . \quad (22)$$

where δ is a constant for that particular specimen of wire. To deduce (22) we proceed as follows :—

$$t - t_{pt} = t - \frac{\alpha t + \beta t^2}{(100)\alpha + (100)^2\beta} \times 100 \text{ from (21) and (19)}$$

$$= -\frac{\beta(100)^2}{\alpha + 100\beta}\left[\left(\frac{t}{100}\right)^2 - \frac{t}{100}\right].$$

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[1] Callendar, *Phil. Trans.*, 178, 160, 1887; Callendar, *Phil. Mag.*, **32**, 104, 1891; Callendar *Phil. Mag.*, 47, 191, 1899.

[2] c is slightly different from α. The exact relation may be deduced to be.

$$\alpha = c\left(1 + \frac{\delta}{100}\right); \ \beta = \frac{-c\delta}{(100)^2}.$$

Thus δ in equation (22) is equal to

$$-\frac{\beta(100)^2}{\alpha+100\beta} \quad . \quad . \quad . \quad . \quad . \quad (23)$$

The value of δ for the specimens employed lies between 1·488 and 1·498. The higher the purity the greater is α and the smaller is δ. δ is determined by finding the platinum temperature t_{pt} for the boiling point of sulphur whose true temperature is known, and then substituting in (22). Later work by Heycock and Neville, and Waidner and Burgess showed that if the platinum thermometer is standardised at 0°, 100° and the boiling point of sulphur the parabolic formula (22) gives true readings as far as 630°C.

1·15. Measurement of Resistance.—The determination of temperature by this thermometer involves the accurate measurement of the resistance of the platinum wire. The measurement should be capable of a high degree of accuracy for the fundamental interval is generally 1 ohm and measurement of temperature to hundredths of a degree requires resistance measurements correct to 1/10,000 ohm. It is therefore essential that the resistance of the connecting leads should be completely eliminated. Three methods (shown in Fig. 8) of compensating for or eliminating the effects of the resistance of the thermometer leads which have been in general use are the Siemens three-lead method,[1] the Callendar's compensating leads method (explained in §1·14), and the potential-terminal method. In the last method measurements are made with a potentiometer, a Thompson bridge or a differential galvanometer. This method is the best because the indications are independent of the resistance of the leads, while in the first two they are not quite independent. It is only when the leads have the same resistance that their resistances balance. The second method is employed in the well-known Callendar and Griffiths bridge which is described below.

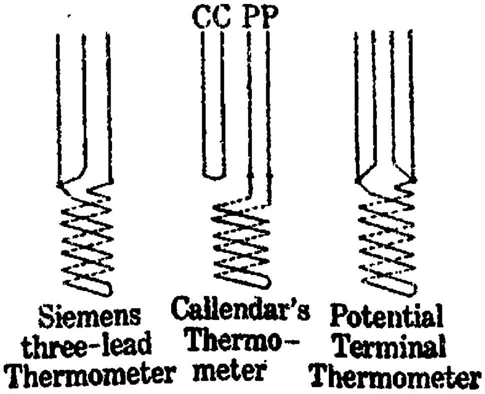
CC PP
Siemens three-lead Thermometer
Callendar's Thermo-meter
Potential Terminal Thermometer

Fig. 8.—Three methods of using a resistance thermometer.

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[1] For details see Mueller, *Bull. Bur. Stand.*, **13**, 547, 1916.

Fig. 9 represents the Callendar and Griffiths bridge[1] diagrammatically. The ratio arms Q and S, are kept equal by the makers of the instrument. R consists of a set of resistances of 1, 2, 4, 8, 16, 32, 64 units. The usual plug contacts are here replaced by mercury cup contacts. L_1, L_2 are two parallel wires of the same material which can be connected to each other by the contact-maker K. This arrangement is adopted in order to eliminate thermo-electromotive forces. P represents the thermometer and C the compensating leads. The bridge is adjusted for no deflection of the galvanometer G. The resistance r acts as a shunt and makes the resistance of the wire L_2 exactly in the desired ratio. Various other bridges have been devised but the one by Mueller[2] in particular is capable of yielding results of the highest precision. Various precautions are generally necessary some of which are given below[3] :—

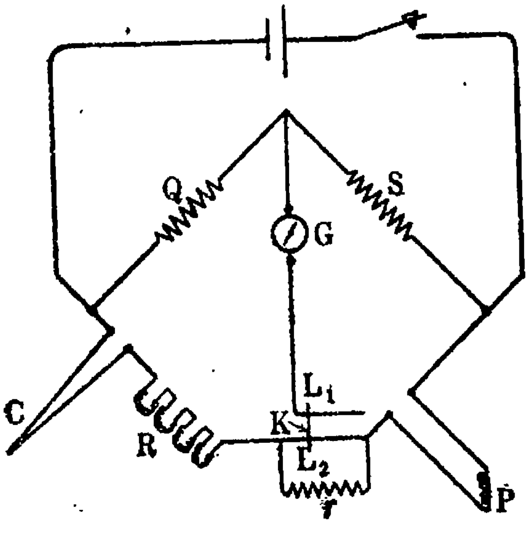

Fig. 9.—Callendar and Griffiths' Bridge.

(1) The current flowing through the bridge heats the bridge coils and changes their resistance. The change in temperature may be observed on a thermometer and the corresponding change in resistance calculated. The correction can then be easily applied. Or the bridge may be placed in a thermostat.

(2) The thermometer coil has to be very thin (·15 mm. diameter) since it must have a large resistance and hence the heating effect is considerable. From Callendar's observations the heating effect for a current of ·01 ampere is 0·016° at 0°C., and 0·017° at 100° C. Further the heating effect does not reach its maximum immediately the battery circuit is completed and the galvanometer indicates a gradual drift. According to Callendar the best procedure is to pass the same current through the thermometer at all temperatures when the heating effect remains approximately constant.

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[1] For further details see Flint and Worsnop, *Practical Physics*.

[2] Mueller, *Bull. Bur. Stand.*, **13**, 547, 1916. Mueller, *Ibid.*, **11**, 57, 1915.

[3] For further details see *Methods of Measuring Temperature*, by E. Griffiths (Chap. 3).

(3) The bridge centre must be determined and the bridge wire calibrated.

(4) Due to temperature gradient along the conducting leads and the junctions thermo-electromotive forces are developed in the circuit whose magnitude may be found by closing the galvanometer circuit when the battery circuit is kept open. To eliminate these, the galvanometer circuit should be permanently closed and balance obtained for reversals of the battery current. If induction effects are perceptible when the battery circuit is made or broken, a thermoelectric key should be employed. This key first breaks the galvanometer circuit, then makes the battery and the galvanometer circuits in succession.

(5) The external leads connecting the terminals PP, CC to the bridge should be exactly similar and similarly placed.

1·16. As already mentioned, the platinum thermometer is standardised by measuring the resistance at the melting point of ice, boiling points of water and sulphur. The last gives δ, and hence t can be determined from any subsequent determination of t_{pt} and then utilising equation (22). For convenience of calculation tables have been prepared giving the gas scale temperatures corresponding to measured platinum temperatures for a standard value of δ. Another table gives the change in the gas scale temperature for a small change in δ. Still, however, equation (22) does not hold much above 630°C. For this reason every platinum thermometer is provided with a calibration curve drawn by an actual comparison with a standard gas thermometer in standardising laboratories. The temperature can be directly read from this temperature-resistance curve. A detailed comparison of platinum resistance thermometer has been carried[1] out at the Bureau of Standards in the temperature range -190°C. to 445°C.

The great advantage of platinum thermometers lies in their wide range (-200°C. to 1200°C.). If carefully prepared, their readings are reliable to 0·02° in the range 0° to 630°C and to 0·1° up to 1200°C. They are free from changes of zero for the wire, when pure and well-annealed, has always the same resistance at the same temperature. They are very convenient for ordinary use, and when once standardised by comparison with a gas thermometer, they serve as reliable standards. They are often employed to measure small *differences* of temperature very accurately, sometimes even to one ten-thousandth of a degree. There are however some drawbacks also. The resistance thermometer has a large thermal capacity and the covering sheath has low thermal conductivity and therefore the thermometer does not quickly attain the temperature of the bath in which it is immersed. Further some time is lost in balancing the bridge. For these reasons the resistance thermometer is useless for measuring rapidly changing temperatures. Further impurities in the platinum are highly detrimental to accurate work. Impure platinum does not obey the same resistance-temperature law as the pure metal. The platinum used for making thermometers should be of such purity that R_{100}/R_0 is not less than 1·390.

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[1] See Hoge and Brickwedde, *Jour. Res. Bur. Stand.*, Washington, **28**, 217, 1942.

Another type of resistance thermometer which has the advantage of very high sensitivity is provided by the *thermistor.* A thermistor consists of a small bead of semi-conducting material which has a very high negative temperature coefficient of resistance varying inversely as the square of the absolute temperature. It has however the serious disadvantage of instability of resistance.

1·17. Differential Platinum Thermometer.—For measuring small differences of temperature very accurately a differential platinum thermometer is sometimes employed. In this there are two resistance coils, each having three leads at its both ends. Through one pair of leads the current is allowed to flow while the second pair is used for the measurement of the potential difference across it and the third pair for connecting a resistance in parallel with it. When the two coils are immersed in two baths having different temperatures, their resistances, R_1 and R_2, become different but by connecting resistances R_1' and R_2' in parallel to them respectively it is so adjusted with the help of a differential galvanometer that the E. M. F. across each coil and consequently the resistances of both become identical. Then

$$\frac{1}{R_1}+\frac{1}{R_1'}=\frac{1}{R_2}+\frac{1}{R_2'}\text{; or } R_2-R_1=R_1R_2\frac{R_1'-R_2'}{R_1'\,R_2'}.$$

Thus knowing R_1, R_2, R_1', R_2' we can calculate the difference R_2-R_1 accurately from which the difference in temperature can be calculated.

THERMO-ELECTRIC THERMOMETRY

1·18. Thermo-Couples.—Let us now return to the second electrical property utilised for temperature measurement. Starting from Seebeck's discovery of thermo-electricity in 1828 numerous attempts were made to construct a thermometer based on this principle, for instance, by Becquerel, Pouillet and Regnault. At present thermo-electric thermometry has attained a degree of precision inferior only to resistance thermometry below about 1000°C. but for temperatures exceeding that, it is the only sensitive and convenient electrical method at our disposal.

A complete thermo-electric thermometer outfit consists of the following parts :—

(1) The two elements constituting the thermo-couple.

(2) The electrical insulation of these wires and the protecting tubes.

(3) Millivoltmeter or potentiometer for measuring the thermo-electromotive force.

(4) Arrangements for controlling the cold-junction temperature.

The choice of the elements constituting the couple is determined by the temperature to which the couple is to be heated and the thermo-electromotive force developed at this temperature. For low temperatures up to 300°C. couples of base metals, such as iron-constantan and copper-constantan are satisfactory, as they develop large E.M.F. of about 40 to 60 microvolts per degree. For high temperatures these base metals cannot be used as they get oxidized and melt. Nickel-iron couple may be used up to 600° while nickel-nichrome and chromel-alumel thermo-couples can be used up to 1000°C., but above that platinum and an alloy of platinum with iridium or rhodium must be used. Le Chatelier in 1886 introduced the couple consisting of pure platinum and an alloy containing 90 per cent Pt and 10 per cent Rh which is now largely employed for scientific work. The E.M.F. developed by these noble metals is, however, rather small.

The two elements are taken in the form of a wire and one end of both is welded together electrically or in an oxy-

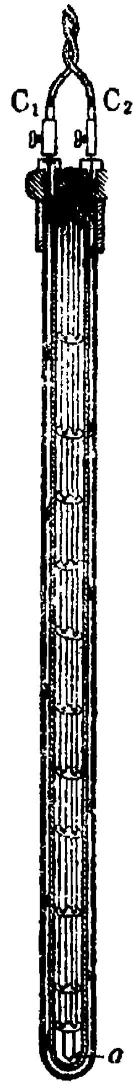
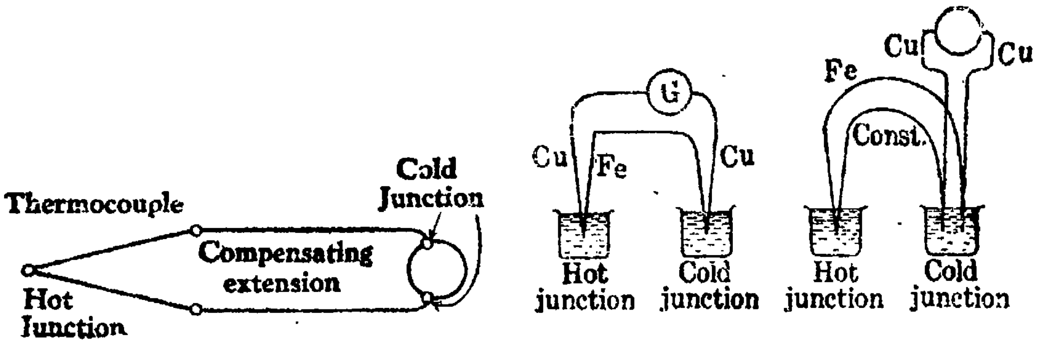


Fig. 10.—Thermo-couple.

hydrogen flame. This end *a* (Fig. 10) forms the hot junction. The portions of the wires near the hot junction are insulated with capillaries of fire-clay (or hard glass for lower temperatures) and are threaded through mica discs enclosed in outer protecting tube of procelain, quartz or hard glass, depending upon the temperature for which it is meant. The protecting tube prevents the junction from contamination but necessarily introduces a lag. For rough use this may be further enclosed in a steel sheath (shown black in the figure). Where there is no risk of contamination, the mica discs and the protecting tubes can be dispensed with. The wires are connected to terminals C_1 and C_2 on the instrument. To these terminals are connected extension leads leading to the cold junction [Fig. 11(*a*)]. For base-metal couples these leads are of the same material as the elements of the couple itself. Thus the cold junction is transferred to a convenient distant place where a constant temperature, say 0°C., can be maintained. Usually the extension leads are marked so that there is no difficulty in connecting to the proper terminals. There are two ways of making the connections which are indicated in Fig. 11 (*b*) and (*c*). For Pt, Pt-Rh couple it is very expensive to use extension leads of these elements and hence leads of copper and nickel-copper alloy may be used, copper being connected to the Pt-Rh wire and nickel-copper alloy to the Pt wire. The



(*a*) (*b*) (*c*)

Fig. 11.—Methods of using a Thermo-couple.

effects produced by these leads almost completely balance provided C_1 and C_2 (Fig. 10) are at the same temperature. The other ends of these leads form junctions with copper wires, the junctions being immersed in melting ice contained in a Dewar vessel to form the cold junction as indicated in Fig. 11(*c*). The E.M.F. developed is measured with a milli-voltmeter or potentiometer. For accurate work the binding screws of the potentiometer must be of copper.

The measurement of E.M.F. is based upon the three fundamental laws of thermo-electricity : (1) the law of the homogeneous circuit, (2) law of intermediate metals and (3) law of intermediate temperatures. The law of homogeneous circuit, established experimentally, states that an electric current cannot be maintained in a circuit of a single homogeneous metal of varying cross-section by the application of heat alone. The law of intermediate metals states that the algebraic sum of the electromotive forces in a circuit composed of any number of dissimilar metals is zero if the entire circuit is at a uniform temperature. The law of intermediate temperatures states that the electromotive force developed by any thermo-couple with its junctions at temperatures T_1 and T_3 is the algebraic sum of the electromotive forces developed with junctions at T_1 and T_2, and at T_2 and T_3. It follows from these laws that the algebraic sum of the thermal electromotive forces developed in any circuit containing any number of dissimilar homogeneous metals depends only upon the temperatures of the junctions.

1·19. To find the temperature of the hot junction we must measure the E.M.F. developed by the thermo-couple. This can be done by means of a high resistance milli-voltmeter which may be graduated to read temperatures directly and the temperature thus obtained can be relied upon to about ±5°C. For attaining higher accuracy a potentiometer must be used.

This arrangement essentially consists of a number of resistance coils A (Fig. 12, p. 32) placed in series with a long wire resistance r stretched along a scale. A current from the battery B flows through these resistances and its strength is so adjusted by varying **R** that the potential difference across a fixed resistance K balances against the E.M.F, of a standard cadmium cell C (1·0183 volts). The E.M.F. developed by the thermo-couple Th is balanced as indicated. The potentiometer can be made direct reading by keeping

K = 101·83 ohms. Thus there is a fall of 1 volt per 100 ohms and by constructing the smallest resistance coil of 0·1ohm resistance and the wire *r* also of the same resistance, the total E.M.F. across the wire will be 1 mV. If the wire is divided into 100 divisions and in addition has a sliding vernier having 10 divisions, the readings can be taken correct to 1 micro-volt.

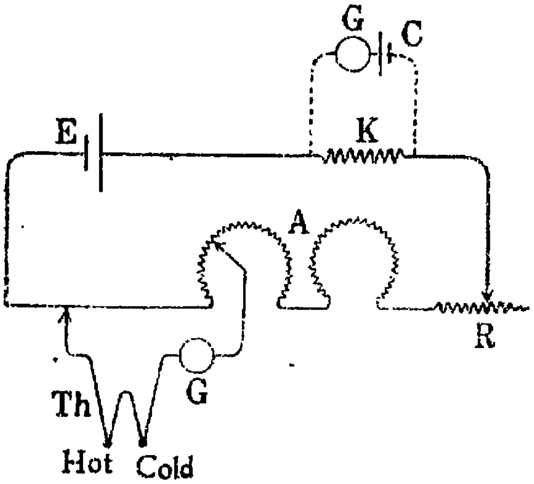


Fig. 12.—Illustration of the principle of potentiometer.

Various types of potentiometers based on this principle have been devised specially for this purpose.[1] With these instruments the E.M.F. can be measured accurately to 1 micro-volt which corresponds to about 0·1°C. for a Pt, Pt-Rh couple. For a copper-constantan couple this corresponds to about 1/40 degree. By using a sensitive moving coil galvanometer and taking sufficient precautions it is possible to measure to 0·1 micro-volt and the sensitiveness is increased about ten times. The sensitiveness can also be increased by using a number of thermo-couples in series.

For accurate work the cold junction must be mantained at 0°C., otherwise corrections[2] will be required.

In order to deduce the temperature from an experimental determination of the E.M.F. a calibration curve is generally supplied with the instrument. This gives the temperature corresponding to different electromotive forces developed and has been drawn by the makers by an actual comparison with a standard thermocouple throughout the range. If it is required to calibrate a thermocouple in the absence of a standard one, the fixed points (§ 1·12) must be utilised. The E.M.F. at those points is measured and an empirical interpolation formula employed in order to give the E.M.F. corresponding to the intermediate temperatures. For a Pt, Pt-Rh couple it is found that three different equations must be used for the different ranges. Thus

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[1] For a description of these see Ezer Griffiths, *Methods of Measuring Temperature*.

[2] See F. Roeser, *Jour. App. Phys.* **11**, 394, 1940.

$$\left.\begin{aligned} &\text{from } 0^\circ \text{ to } 400^\circ\text{C., } E = At + B(1 - e^{ct})\,; \\ &300^\circ \text{ to } 1200^\circ\text{C., } E = -A' + B't + C't^2\,; \\ &1100^\circ \text{ to } 1750^\circ\text{C., } E = -A'' + B''t + C''t^2 \end{aligned}\right\} \quad . \quad . \quad (24)$$

where A, B, C, are constants whose values are determined empirically.

The average value of these constants have been found from experiments on different specimens and from these a table giving the temperature for different E.M.F's has been prepared. In practice it is, therefore, found convenient to determine the E.M.F. of the thermo-couple (required to be used) at a few fixed points and then draw a 'difference curve' giving the difference of readings of this thermo-couple and the tabulated[1] values of a thermo-couple of the same group in terms of the experimental thermo-couple. From this 'difference curve' the true E.M.F. and then from the table the corresponding temperature is found out.

Thermo-couples are frequently employed for laboratory work since they are cheap and can be easily constructed. They can be used for the measurement of rapidly-changing temperatures since the thermal capacity of the junction is small and hence the thermometer has practically no lag. Another advantage in the use of thermo-couples is that they measure the temperature at a point —the point at which the two metals make electrical contact. Its chief disadvantage lies in the fact that there is no theoretical formula which can be extrapolated over a wide range and consequently every thermo-couple requires separate calibration.

The useful range of thermo-electric thermometers is about –200°C. to 1600°C. though couples of Ir and 90 per cent Ir 10 per cent Ru have been used up to 2100°C. Readings are reliable only when the composition of the couple does not change even slightly. In actual practice frequent calibration is necessary.

The following are the chief sources of error in thermo-electric thermometry :—

(1) Parasitic electromotive forces developed in the circuit. They are due to (*a*) Peltier effect or E.M.F. developed due to heating of junction of dissimilar metals at points of the circuit other than the hot and the cold junctions. This occurs often in the measuring apparatus. (*b*) Becquerel effect or E.M.F. generated due to inhomogeneities in a single wire; this occurs mainly in the thermo-couple wires. The E.M.F.

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[1] Such tables for Pt, Pt-Rh and Cu-constantan have been published by Adams in *Symposium on Pyrometry*, Amer. Inst. of Mining and Metall. Engineers, September, 1919, p. 165.

measured is a sum of the effects (*a*) and (*b*), and the Peltier E.M.F. at the two junctions and the Thomson E.M.F. along homogeneous wires of the thermocouple with ends at the two temperatures. The undesirable effects mentioned in (*a*) and (*b*) must be eliminated by the use of materials and methods free from these effects since they are not taken into account in any thermo-electric formulæ.

(2) Leakage from the light mains or furnace circuit. If leakage currents pass through the potentiometer their presence can be detected by short-circuiting the thermo-couple when the galvanometer continues to be deflected.

(3) Cold-junction correction if it is not kept at 0°C.

For the methods of minimising or eliminating these errors the reader is referred to *Measurement of High Temperatures* by Le Chatelier and Burgess.

We give below in table 4 the thermo-electric force for various couples in common use. The cold junction is maintained at 0°C.,

Table 4.—E.M.F. in millivolts for some common couples.

Temp. °C.	90% Pt 10% Rh against Pt[1]	Chromel/ Alumel	Chromel/ Constantan	Iron/ Constantan[2]	Copper/ Constantan[2]
−183	..	−5·48	−8·25	−7·83	−5·26
−80	..	−2·87	−4·26	−3·93	−2·76
0	0·000	0·00	0·00		0·00
100	0·643	4·10	6·32	5·40	4·276
200	1·436	8·13	13·42	10·99	9·285
400	3·250	16·40	28·95	22·07	20·365
600	5·222	24·91	45·10	33·27	..
800	7·330	33·30	61·08	45·69	..
1000	9·569	41·31	..	..	..
1200	11·924	48·89	..	..	..
1400	14·312	..	..	..	..
1600	16·674	..	..	..	..
1700	17·841	..	..	..	.

while the hot junction is at t°C. If the current flows from metal A to metal B at the cold junction, A is said to be thermo-electrically positive to B, and the E.M.F. of the thermo-couple AB will be positive and that of BA negative. Rare-metal couples of good manufacture will reproduce the values given in the reference table to within about ±1°C. at the gold point or ±3°C. at the top of the range.

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[1] *Bur. of Stand. J. of Research*, **10**, 275, 1933. See also C. R. Barber, *Proc. Phys. Soc. Lond.*, B., **63**, 492, 1950.

[2] *Bur. of Stand. J. of Research*, **20**, 337, 1938.

1·20. Differential Thermo-couples.—For measuring very small differences of temperature accurately sometimes differential thermocouples are used. Fig. 13 shows such a thermocouple. A single wire B of some metal forms the one element of both the couples, while the other elements of the two couples consist of wires A_1 and A_2 of another substance. These are joined at J_1 and J_2 to two copper leads connected to the millivoltmeter V or potentiometer. The junctions H_1 and H_2 are immersed in the baths whose difference of temperature is required, while J_1 and J_2 are maintained at 0°C. It is seen that the E.M.F.s developed by the two couples oppose each other. The net E.M.F. developed is equal to

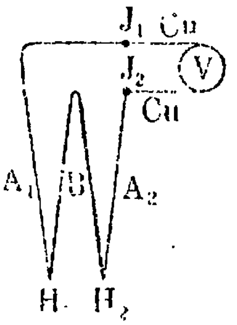

Fig. 13.—Differential thermo-couple.

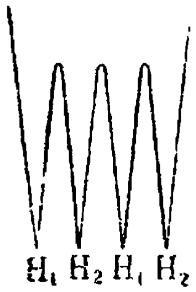

Fig. 14.—A number of differential thermo-couples:

$$(T_2-T_1)\ (dE/dT)_{T_1}^{T_2}$$

where T_1 and T_2 denote the temperatures of H_1 and H_2 respectively and $(dE/dT)_{T_1}^{T_2}$ denotes the rate of variation of the E.M.F. for the two elements between the temperatures T_1 and T_2. Thus the difference in temperature (T_2-T_1) can be found if the variation of the E.M.F. for the couple is known. For greater sensitivity a number of such couples are used as shown in Fig. 14. It will be seen that the alternate junctions are all immersed in the bath at T_1 and the rest in T_2.

1·21. Certain methods of measuring temperature utilise the radiation emitted by the hot body whose temperature is to be measured. These methods will be discussed in detail later (Chap. XV). They are generally used for measuring temperatures from about 1000°C. to any upper limit.

Another type of thermometer generally employed for low temperature work is the *vapour pressure* thermometer. In this, the vapour pressure exerted by the liquid at different temperatures is measured. Now since the vapour pressure of a liquid increases with rise of temperature it is clear that the temperature can be easily deduced from a measurement of the pressure exerted by the saturated vapour. A vapour pressure thermometer is described in section 1·24.

1·22. Other methods which have been utilised for measuring temperature make use of one of the following properties of matter :—

(1) Expansion of a bar of metal.
(2) Paramagnetic susceptibility of salts (Chap. XII).
(3) Changes in vapour density with rise of temperature.
(4) Variation of refractive index of a gas with temperature in accordance with Gladstone and Dale's law.
(5) Calorimetric methods based on the measurement of quantity of heat.

1·23. Low Temperature Thermometry[1].—The standard thermometer in this range is the constant volume hydrogen or helium thermometer. The difficulty in this case is that gases liquefy and even solidify at these low temperatures. Prof. Dewar, however, showed that the boiling point of hydrogen as indicated by the hydrogen thermometer was −253·0°C. and −253·4°C., while a helium thermometer registered −252·7°C. and −252·1°C. Similarly, he compared thermometers of other gases .These experiments evidently led to the conclusion that a gas could be relied upon even to its boiling point. Thus helium furnishes the scale down to its boiling point (4·2°K). The corrections necessary to convert this scale to the thermodynamic scale may be obtained as in §1·7 and have been given by Onnes and Cath[2] (see table 1 § 1·8). For temperatures below 4·2°K we must use the helium gas thermometer with the pressure well below the vapour pressure of liquid helium at the temperature to be measured. In some recent determinations Schmidt and Keesom used initial pressures of 0·0665 cm. of mercury (at 4·2°K) in the gas thermometer. The exact measurement of these very low pressures involves considerable experimental difficulties chiefly on account of adsorption of helium by pyrex glass and the thermo-molecular effect (Chap. III). Due to the latter effect the pressure measured by a manometer kept at room temperature may be appreciably greater than the pressure in the thermometer bulb. For pressures greater than about 1 cm. of mercury this effect can be neglected but for lower pressures corrections must be applied to take it into account. A hot wire manometer is often used to measure this pressure and is placed very close to the thermometer. With these devices the helium gas thermometer gives us the thermodynamic scale down to 1°K. Below this it is difficult to fix the thermodynamic scale with certainty. Now we shall consider the secondary standards.

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[1] See Burton, Smith and Wilhelm, *Phenomena at the Temperature of liquid helium* (1940), Chaps. III and VIII.

[2] *Leiden Commun.*, No. 156 (a), 1922.

Mercury freezes at −38·87°C., and alcohol at −111·8°C. and hence these thermometers cannot be used below the respective temperatures. A special liquid thermometer containing fractionally distilled petroleum ether can be used down to −190°C.

But for all accurate work, however, *resistance thermometers* are employed. It is absolutely essential that the substance of which the thermometer is made is perfectly pure. Pure metals show a regular decrease in resistance with decrease of temperature. Dewar and Fleming found that the presence of the slightest trace of impurity in a metal is sufficient to produce a considerable increase in resistance at these low temperatures. It is, therefore, difficult to trust the purity of any specimen for very low temperatures without actual comparison. Henning[1] found from a detailed investigation that the parabolic formula did not hold below −40°C. Van Dusen[2] proposed the formula

$$t = \frac{R_t - R_0}{R_{100} - R_0}\,100 + \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} + \epsilon\left(\frac{t}{100} - 1\right)\frac{t^3}{100^3}, \quad . \quad (25)$$

where ϵ is a constant and δ has already been defined in §1·14. The constants R_0, R_{100} and δ are determined by calibration at 0°C., 100°C. and the boiling point of sulphur as explained previously, and the constant ϵ is then determined by calibration at the boiling point of oxygen[3] which is taken as −182·97°C. The method of using it is, as before, to calculate the platinum temperature and to use its value in (25) to get the difference formula and apply successive approximations to get the correct difference $t - t_{pt}$.

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[1] *Ann. d. Physik*, **40**, 635, 1913.

[2] *Journ. Amer. Chem. Soc.*, **47**, 326, 1926.

[3] See Heuse and Otto, *Ann. d. Physik*, **9**, 486, 1931; Yost, Garner Osborne, Rubin and Russel, *Journ. Amer. Chem. Soc.*, **63**, 3488, 1941.

Van Dusen's formula has been found to hold satisfactorily from 0°C. to −190°C., the error now here being greater than ±0·05°.

For temperatures below −190°C. the platinum resistance thermometer has been used by Henning and Otto[1] who have given a complicated formula[2] for calculating temperatures from the observed resistance. The formula is, however, not entirely satisfactory and hence it cannot be used to calibrate the platinum thermometer from the fixed points alone. The procedure generally adopted is to select a particular platinum thermometer and calibrate it by actual comparison with a standard gas thermometer. Values of R_T/R_0 are thus determined at different temperatures, R_T being the resistance at the temperature T. Such a table of values from 10° to 95°K has been given by Hoge and Brickwedde.[3] Since no two samples of platinum have exactly the same resistance temperature relation, the table applies directly only to one platinum thermometer. For other thermometers a deviation curve must be drawn showing the difference between their resistance ratios and that of the standard, the points being determined by calibration at a few temperatures. For details see the paper by Hoge and Brickwedde. Resistance thermometers of lead have also been employed in this region. Onnes[4] used a lead resistance thermometer down to −259°C. He actually found the resistance of a lead wire at various temperatures as observed on a gas thermometer. Nernst[5] gave a method of using the readings of Onnes for calculating temperatures with the help of any other lead thermometer.

For temperatures below about 20°K, the normal boiling point of hydrogen, the platinum resistance thermometer is not sufficiently sensitive. Pure lead makes a reasonably sensitive resistance thermometer down to 7°K but the best metals for the purpose are the alloys constantan and unannealed phosphor-bronze since they have large temperature coefficient, but their usefulness is somewhat limited by the fact that their resistance is increased by an external magnetic field. Thermometers of phosphor-bronze are much more sensitive since their temperature coefficient of resistance is fifty-five times greater than that of constantan. Further, the resistance changes linearly with the temperature and is much less affected by magnetic fields. Phosphor-bronze can be used down to 0·03°K but its resistance depends to some extent on the strength of the current used to measure it. Constantan thermometers do not appreciably suffer from this difficulty and give a smooth calibration curve from 20°K to 2°K. Recently carbon resistance thermometers have been utilised below 1°K since their resistance *increases* very rapidly as the absolute zero is approached. All resistance thermometers for use below 5°K must be calibrated by means of a helium vapour pressure thermometer.

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[1] *Phys. Zeits.*, **37**, 639, 1936.

[2] The formula is $R_T/R_0=a+(bT+cT^2)D(d100/T)+(d+eT-cT^2)D(230/T)$ where T is the absolute temperature and D denotes the Debye specific heat function (Chap. XVI).

[3] *Bur. of Stand. J. of Research*, **22**, 351, 1939.

[4] *Leiden Commun.*, No. 99, 1907.

[5] Nernst, *Grundlagen des neuen Wärmesatzes*, p. 31.

For low temperatures copper-constantan and iron-constantan *thermocouples* are convenient to use as they develop a large E.M.F. They are very sensitive up to —200°C. and can be used down to —255°C. Below —200°C., however, couples of gold-silver and platinum-silver are preferable. For very low temperatures an alloy of gold with about 2 per cent. cobalt against the standard silver alloy (containing 0·37 atomic per cent. of copper) is found to be quite sensitive and has been used from 17 to 2·5°K.

The helium gas thermometer and the vapour pressure thermometer (§1·24) have been used down to 0·75°K but for temperatures lower than this the paramagnetic susceptibility of certain salts has been utilised (Chap. XII). For this it is necessary to assume that the paramagnetic susceptibility varies inversely as the absolute temperature—a law which is known to fail very near the absolute zero.

1·24. Vapour Pressure Thermometers.—We have considered above two types of secondary thermometers which are used in low-temperature work—resistance thermometer and thermo-couple. The third type is the vapour pressure thermometer whose principal advantage is its high sensitivity in certain temperature intervals. Its use is based on the well-known fact that the vapour-pressure of a liquid varies uniquely with the temperature (Chap. XI). To every temperature there corresponds a fixed vapour pressure which is less for lower temperatures. The method consists simply in measuring the vapour pressure of a certain liquid at the required temperature. Fig. 15 shows a vapour pressure thermometer of the type used at Leiden. It consists of a small bulb a containing the liquid and connected with capillaries b, c to the manometer mm' while M is a mercury reservoir for raising or lowering the mercury level in m, m'. The bulb a and a part of the glass capillary b are surrounded by a copper tube e in order to ensure uniformity of temperature, while b is further surrounded by a glass tube g closed at the top. This latter prevents radiation of heat to and from the tube. For setting up the apparatus, the mercury level in m is lowered, the vessel a and the connecting tubes are evacuated through t, and finally the desired gas is also introduced through t. Next, the gas is compressed by raising the reservoir M and a part of it becomes liquefied in a. Then the globe a and a part of the tube are immersed in the liquid bath whose temperature is to be measured, and the pressure in the manometer mm' is observed. With the help of tables giving the vapour pressure of the liquid at various thermodynamic temperatures, the temperature corresponding to any observed reading of the manometer can be found. These tables are prepared by actually finding the vapour pressure at different temperatures as observed on a gas thermometer. (For a set of such tables see *Handbuch der Physik*, volume IX, p. 590.) The useful liquids are SO_2, ammonia, CO_2, C_2H_4, CH_4, O_2, H_2 and helium.

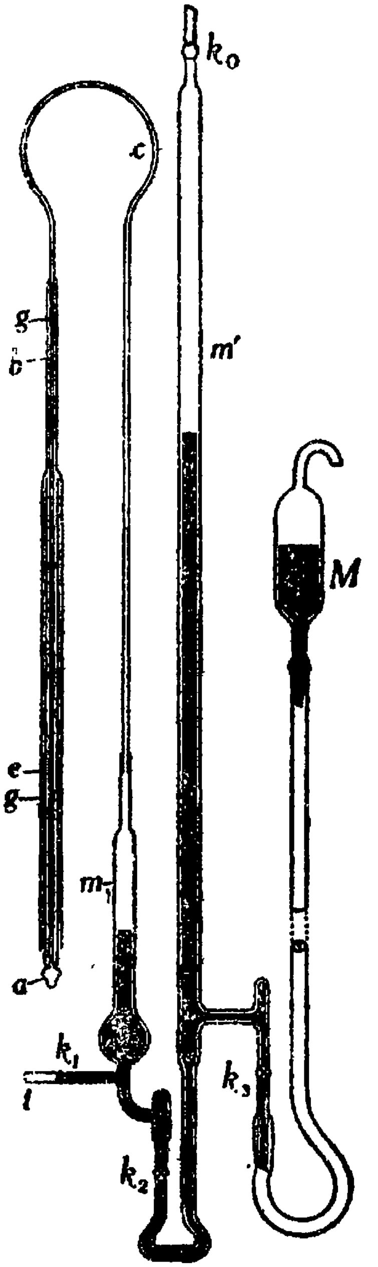

Fig. 15.—Vapour pressure thermometer.

The great disadvantage of these thermometers is that their range is very limited. Oxygen is useful in the range—150°C to −210°C, neon in the range −246° to −249°, hydrogen in −253° to −262° and helium below about −268°C. This is because above these higher limits the pressure is too high for convenient measurement, while below the lower limit, the pressure is too small to be measured accurately. Still however they are frequently used on account of their simplicity and high sensitivity since the vapour pressure curves are very steep near the normal boiling point of these gases. In using these thermometers it is necessary to see that all points in contact with the thermometer tube shall be warmer than the point to be measured since this thermometer always shows the temperature at the coldest point of the apparatus. As mentioned earlier, for pressures below 1 cm. of mercury the pressure in the bulb and in the manometer will be different due to thermo-molecular effect and corrections must be applied for this. These pressures are measured by a liquid manometer, mercury or, for still lower pressures, butyl thallate being used.

The helium vapour pressure thermometer has been used down to 0·75°K, the pressure being measured by a McLeod gauge or a hot-wire manometer. Accurate experimental data regarding the vapour pressure of helium at different temperatures, as measured on a helium gas thermometer, have been obtained by Keesom and his coworkers.[1] They have expressed their results in terms of formulae which constitute the so-called 1932 temperature scale and the 1937 temperature scale. Schmidt and Keesom gave the 1937 scale in the form of a graph of corrections to the 1932 scale but Keesom and Lignac[2] represented it by the following formulae:

Above 2·19°K.

$$\left.\begin{aligned} \log_{10} p &= -\frac{4\cdot7921}{T} + 0\cdot00783T + 0\cdot017601T^2 + 2\cdot6730, \\ \log_{10} p &= -\frac{4\cdot7948}{T} + 0\cdot0343 \log_{10} T + 0\cdot018024T^2 + 2\cdot6775 \end{aligned}\right\}, \quad (26)$$

Between 2·19 and 1·6°K.

$$\log_{10} p = -\frac{3\cdot1189}{T} + 2\cdot5 \log_{10} T - 5\cdot981 \times 10^{-5}\, T^8 + 1\cdot1958, \quad (27)$$

In these formulae p is the vapour pressure expressed in cm. of mercury at the ice-point. Several discrepancies were, however, found in this scale, and consequently Bleaney and Simon[3] suggested the following formula:

$$\log_{10} p = -\frac{3\cdot117}{T} + 2\cdot5 \log_{10} T + 1\cdot196 + \Delta, \quad . \quad . \quad (28)$$

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[1] Keesom, Weber and Nogaard, *Leiden Commun.*, No. **202*b*** (1929); W. H. Keesom, *Leiden Commun.*, *Supp.*, No. 71*d* (1932); Schmidt and Keesom, *Leiden Commun.*, No. 250*c* (1937); *Physica*, **4**, 971, 1937.

[2] *Leiden Commun. Supp.*, No. 90*c* (1939).

[3] *Trans. Faraday Soc.*, **35**, 1206, 1939.

where Δ is a small correction term, its value being given by a graphical representation.

Due to these difficulties the temperature scale in the helium range was discussed recently at a conference in Amsterdam in 1948 and a temperature scale in terms of vapour pressure of the helium isotope of mass 4 has been agreed upon for use in cryogenic laboratories. It is based on eqn. (28) for temperatures below 1·6 °K, and on equations (27) and (26) in their respective ranges but for temperatures between 4·3°K and 5·2°K the data of K. Onnes and Weber[1] are utilised, which can be represented by the interpolation formula:

$$T = 2{\cdot}967 + 1{\cdot}905 \times 10^{-2} p - 3{\cdot}521 \times 10^{-5} p^2. \qquad (29)$$

This agreed temperature scale is given in Table 5 in an abridged form.

Table 5.—Vapour pressure of He⁴ at different temperatures in mm. of mercury at 20°C.

T°K	p (mm)	T°K	p (mm)
0·10	$3{\cdot}4 \times 10^{-32}$	2·50	76·92
0·50	$1{\cdot}6 \times 10^{-5}$	3·00	181·2
0·80	$1{\cdot}1 \times 10^{-2}$	3·50	353·4
1·00	0·121	4·00	615·6
1·50	3·593	4·212	760
2·00	23·45	4·50	980
		5·00	1460

The different thermometers suitable in the different low temperature ranges are represented diagrammatically in Fig. 16 where for convenience of representation the logarithmic scale has been adopted. The ranges of the different vapour pressure thermometers and of the different resistance thermometers are clearly indicated in the figure.

PYROMETRY

1·25. Gas Pyrometers[2].—We have already described the constant-volume hydrogen thermometer with a platinum-iridium bulb. For temperatures above 500°C. hydrogen cannot be used as a thermometric gas because heated platinum is permeable to it, hence nitrogen is invariably employed. As regards the material of the bulb, Jena glass can be used to about 500°C.

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[1] *Leiden Commun.*, 147 *b* (1915).

[2] A good account of high temperature work will be found in an article by Day and Sosman on "The Realization of the Absolute Scale of Temperature" in *A Dictionary of Applied Physics* (Glazebrook), Vol. I,

while quartz glass can stand up to about 1300°C. but is attacked by traces of alkali from hand, etc. Ordinary porcelain is porous and permeable to the thermometric gas but glazed porcelain was formerly employed upto about 1000°C., above which, however, the glazing softens and breaks; also its expansion is not regular. An alloy of platinum and iridium was employed by Holborn and Valentiner upto 1600°C. Iridium, however, distils and also makes the bulb brittle. Holborn and Day found the alloy of 80Pt-20Rh best for the purpose and used a modified form of bulb of this material to about 1600°C. They performed experiments with great care and took into account twentyfive possible sources of error so that their values are regarded as standard at high temperatures. The corrections, which have been discussed in section 1·6, however, become enormous at these high temperatures and hence there is considerable uncertainty in determining the high temperature fixed points with a gas thermometer. Accurate work by Holborn and Day and by Day and Sosman with a gas pyrometer enables us to fix the temperature of the melting point of gold as 1063°C.±0·5 and this "gold point" is largely the basis for our present high-temperature scale. The nitrogen constant-volume scale has been extended up to 1550°C. by Day and Sosman in their monumental work on the determination of the melting point of palladium.

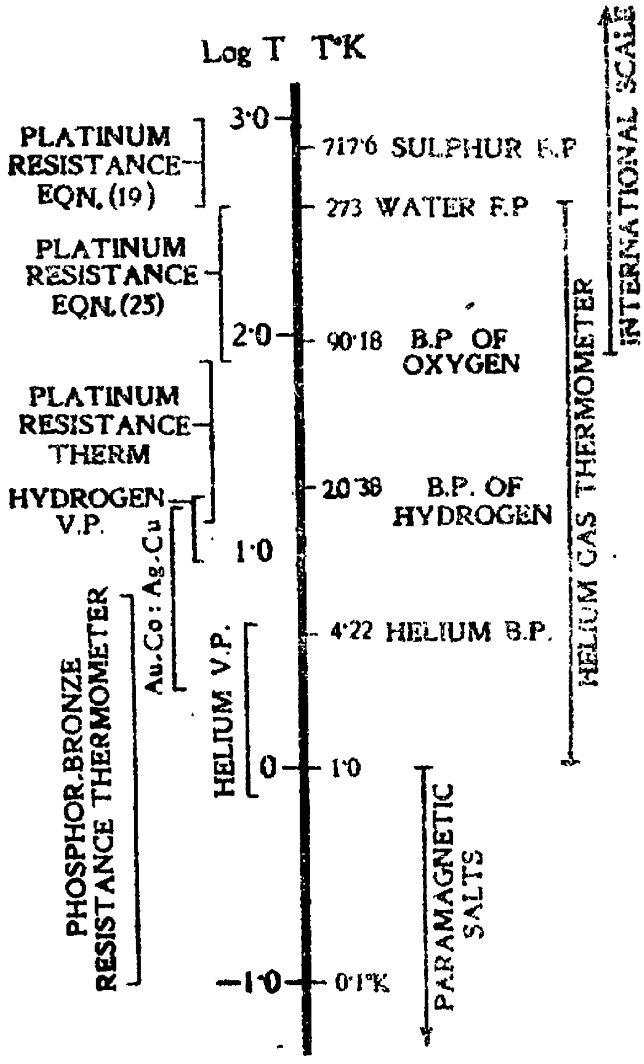

Fig. 16.—The logarithmic scale of temperature.

1·26. Resistance Pyrometers.—The platinum resistance pyrometer has been described above. It can be used to about 1200°C., though the melting point of platinum is 1770°. If used above 1200° the platinum becomes changed and does not return to its initial zero, and has to be restandardised. The mica insulation also sometimes breaks due to moisture getting inside. Up to about 1000°C. it is the most sensitive and useful pyrometer but above 660°C. a calibration curve must be used.

1·27. Thermo-Electric Pyrometers.—The thermo-electric pyrometers have been described above. For temperatures above 600°C. the platinum, platinum-rhodium (90%Pt, 10%Rh) couple is most suitable on account of its good reproducibility and can be used up to the melting point of platinum (1769°C.). It is free from parasitic disturbances and changes in composition, and is the most sensitive pyrometer in the range 1000° to 1500°C. Sometimes the 13%Rh 87%Pt alloy couple is preferred to the 10% alloy as the e.m.f. developed is a little higher. Hoffmann[1] and others have constructed thermo-couples of Ir, 90Ir-10Ru which can be used to about 2100° and possess a sensitivity of 2 micro-volts per degree. For use up to 3000°C. thermocouples of tungsten and an alloy of tungsten with 25 per cent. molybdenum have been constructed by Pirani and Wangenheim[2] which possess a sensitivity of 6 micro-volts per degree at 3000°. Above 1000°C., however, radiation pyrometers are generally used which will be described in Chapter XV.

1·28. International Temperature Scale.—We have seen that the thermodynamic centigrade scale is the standard scale of temperature and is given by the helium or nitrogen gas thermometer, but gas thermometry involves many experimental difficulties. On account of these difficulties in the practical realisation of the thermodynamic scale the International Committee[3] in 1927 found it expedient to adopt a practical scale known as the International Temperature Scale. This scale agrees with the thermodynamic scale as closely as our present knowledge permits and is at the same time designed to be easily and accurately reproducible. It is based upon a number of reproducible fixed points to which numerical values have been assigned and the intermediate temperatures have been defined by agreement as the values given by the following thermometers according to the scheme given below :—

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[1] *Zeits. f. Physik*, **37**, 142, 1926; **27**, 287, 1924.

[2] *Zeits. f. techn. Physik*, **6**, 358, 1925.

[3] For details of the report see paper by Wensel in the *Temperature Symposium* (1939), *loc. cit.* p. 21.

(1) *From* 0°*C. to* 660°*C.*—The standard platinum resistance thermometer calibrated at 0°, 100°C. and the boiling point of sulphur (444·60).

(2) *From* – 190°*C. to* 0°*C.*—The platinum resistance thermometer which gives temperature by means of the formula

$$R_t = R_0\{1 + \alpha t + \beta t^2 + \gamma(t-100)t^3\}, \quad . \quad . \quad (30)$$

the constants being determined by calibration at ice, steam and sulphur points and at the oxygen point (–182·97). It will be seen that this formula is equivalent to van Dusen's formula (25) if $\epsilon = (100)^2\delta\gamma/\beta$. The thermometer must have in addition R_t/R_0 less than 0·250 for $t = -183$°C.

(3) *From* 660°*C to* 1063°*C.*—The platinum Pt-Rh thermocouple where temperature is defined by

$$E = a + bt + ct^2, \quad . \quad . \quad . \quad . \quad (26)$$

and the three constants are determined by calibration at the freezing point of antimony and at the silver and gold points.

(4) *Above* 1063°*C.*— An optical pyrometer (See Chap. XV) calibrated at the gold point (1063°C).

It should be emphasized that the International scale does not replace the thermodynamic scale; it merely serves to represent it in a practical manner with sufficient accuracy for most purposes.

1·29. Illustration of the Principles of Thermometry. –

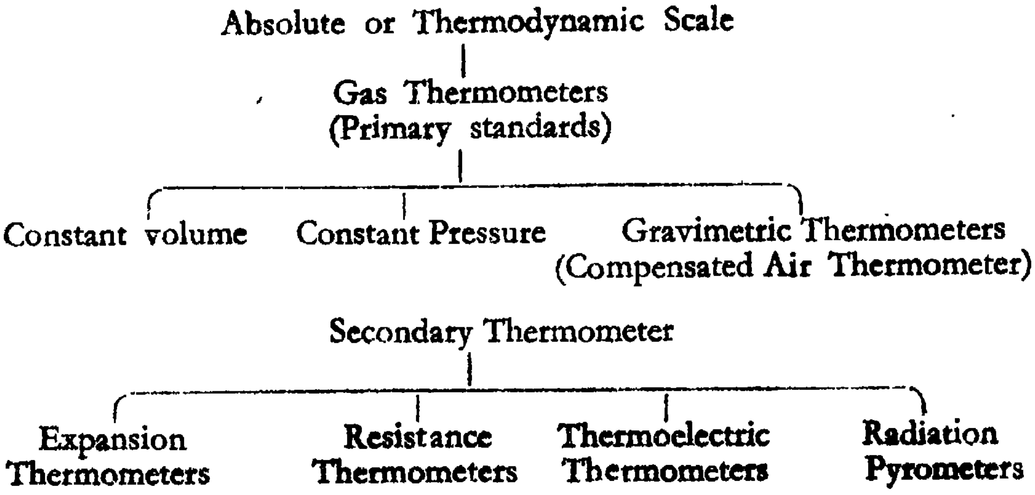


Chart of Fixed Points

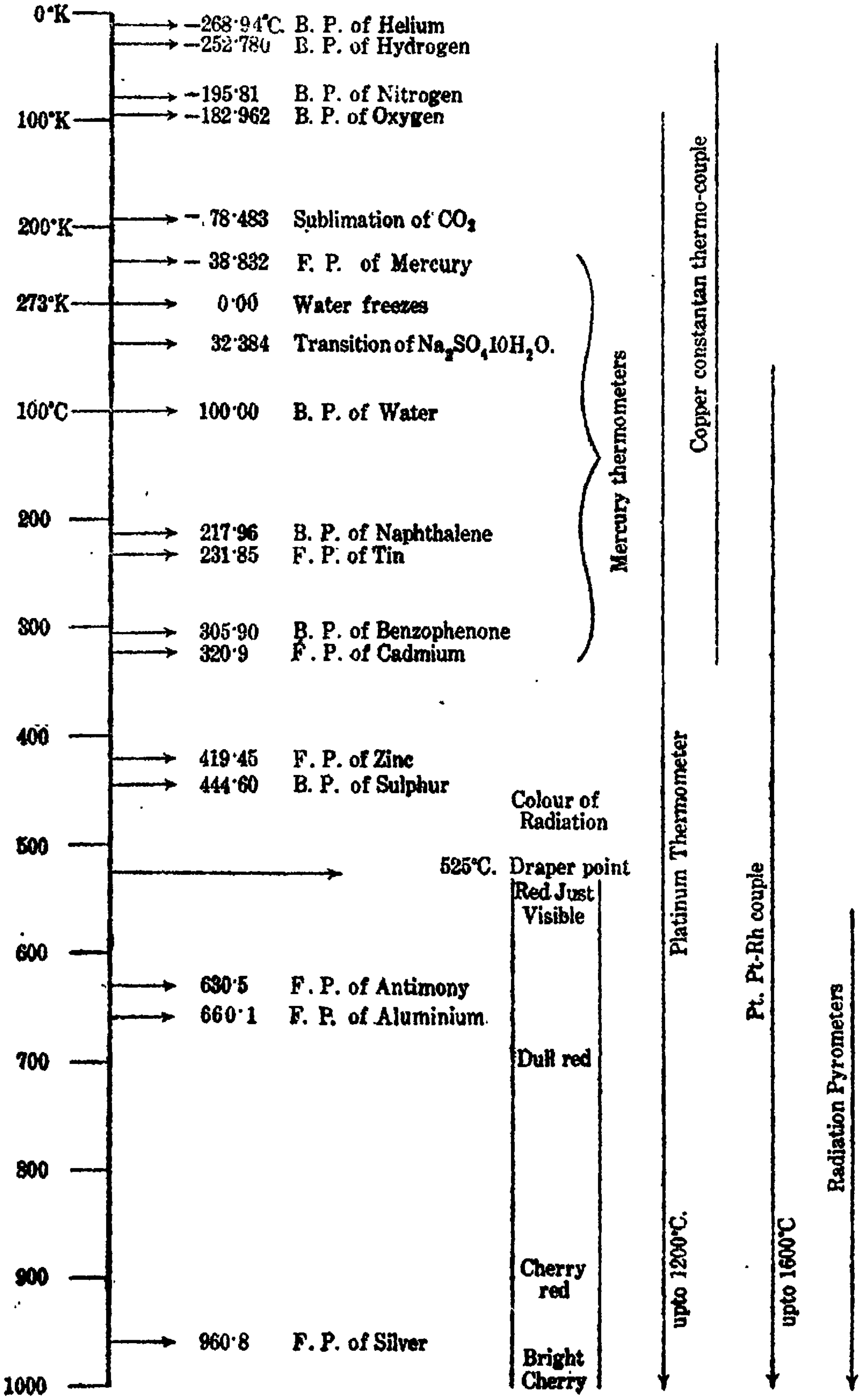
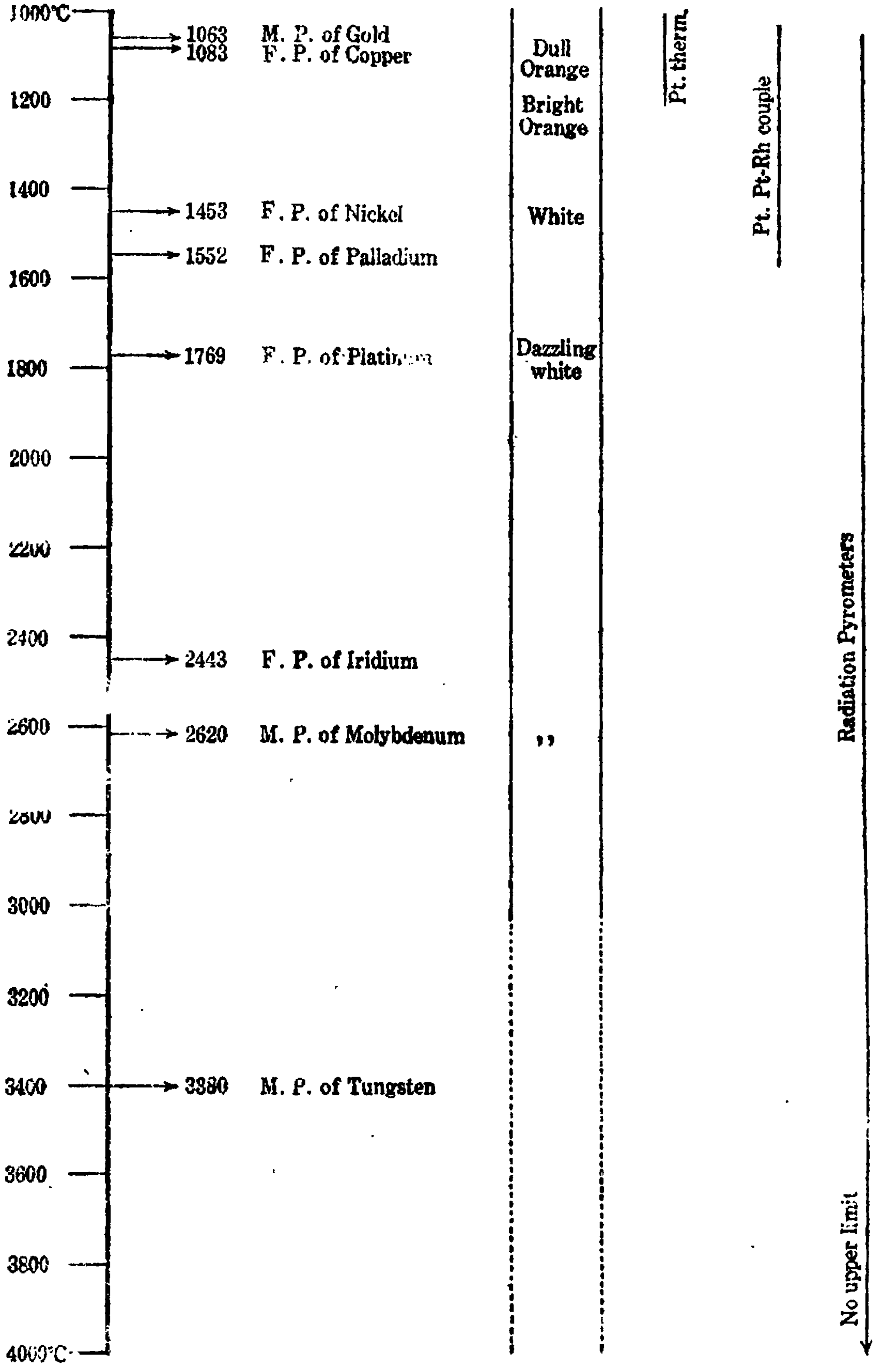


Chart of Fixed Points (Contd).



PROBLEMS

1. The resistance of a platinum thermometer at 0°, 100° and the boiling point of sulphur (444·6°) is 2·56, 3·56 and 6·78 ohms respectively. Calculate the true temperature when the resistance of the thermometer is 5·56 ohms. If the resistance at the boiling point of oxygen (—183·0°C.) is 0·630 ohms, calculate the temperature when the resistance is 1 ohm.

2. Use equation (27) to calculate the temperature when the pressure recorded by a helium vapour pressure thermometer is 10 mm. of mercury.

Books Recommended

1. Burgess and le Chatelier, *The Measurement of High Temperatures.*
2. Ezer Griffiths, *Methods of Measuring Temperature* (Griffin, 1947).
3. Henning—*Temperatur-messung.*
4. *Handbuch der Physik*, **9**, Chap. VIII.
5. Müller-Pouillet's *Lehrbuch der Physik*, vol. 3, part 2.
6. J. A. Hall, *Fundamentals of Thermometry*, Institute of Physics, London (1953).
7. J. A. Hall, *Practical Thermometry*, Institute of Physics, London (1953).
8. Burton, Smith and Wilhelm, *Phenomena at the Temperature of Liquid Helium*, Reinhold Publishing Corporation, New York (1940).
9. *Temperature, its Measurement and Control in Science and Industry* (1941), published by Reinhold Publishing Corporation, New York.
10. *Journal of Applied Physics*, vol. 11, (1940).

CHAPTER II

CALORIMETRY

2·1. Unit Quantity of Heat—The Calorie.—It is a matter of common experience that when a hot body is placed in contact with a cold one, the former becomes colder and the latter warmer ; we say that a certain quantity of heat has passed from the hot body to the cold one. If we take equal quantities of water in three different vessels at the same temperature and plunge equal masses of aluminium, lead and copper previously heated to 100°C. into these vessels, one in each, the equilibrium temperature is highest for aluminium and least for lead. This indicates that, of these three metals, aluminium can yield the largest quantity of heat and lead the least, and we say that aluminium has a larger capacity for heat than lead.

For measuring quantities of heat we require a 'unit'. The quantity of heat required to raise the temperature of 1 gram of water through 1°C. is different for different initial temperatures as we shall see later in this chapter. Hence the unit quantity of heat must be defined with respect to a particular temperature. The International Union of Pure and Applied Physics (1934) recommends the selection of the 15° *calorie* as the standard and defines it as "the amount of heat required to raise the temperature of one gram of water[1] from 14·5° to 15·5° on the International Scale of temperature under the pressure of one normal atmosphere. Another unit sometimes adopted is the *mean centigrade calorie* which is defined to be 1/100th of the total quantity of heat required to raise 1 gram of water from 0°C. to 100°C. The mean calorie is experimentally found to be 1·0002 times the 15° calorie. In Britain the British thermal unit (written B. Th. U.) is frequently employed[2] which represents the quantity of heat required to raise 1 lb. of water through 1°F.

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[1] The specific heat of $H^1{}_2O^{16}$ at 15°C. is 0·99999 of that of normal water. This reduction almost balances the increase in the size of the degree which would result if $H^1{}_2O^{16}$ were selected as the standard substance. Hence the value of the calorie defined in terms of $H^1{}_2O^{16}$ or of normal water agree to about one in a million.

[2] Recently, the joule (10^7 ergs) has been recommended by international agreement for adoption as the unit of heat (See Chap. III for relation between calorie and joule).

2·2. Specific Heat.—The *specific heat*[1] of any substance is defined as the number of calories required to raise 1 gram of the substance through 1°C. This has not the same value at all temperatures. Thus if a quantity of heat Q raises the temperature of m grams of a substance from θ to θ', s the mean specific heat of the substance between θ and θ' is given by $Q/[m(\theta'-\theta)]$; while if the quantity dQ raises the temperature by the small amount $d\theta$ the specific heat at the temperature θ is equal to $(1/m)dQ/d\theta$. The *thermal capacity or water equivalent* of a body is equal to the product of its mass and specific heat.

From the foregoing definitions it follows that if we determine the mean specific heat between 0 and t°C. for various values of t, we can easily calculate the true specific heat at any temperature. Assume that the mean specific heat $\bar{s}$ can be represented by the relation

$$\bar{s} = a\times bt+ct^2\times \ldots, \qquad (1)$$

where t is in degrees centigrade and a, b, c, . . . are constants determined experimentally. Hence the true specific heat s at any temperature t will be given by the relation

$$s = \frac{d}{dt}(\bar{s}t) = a+2bt+3ct^2+\ldots \qquad (2)$$

Thus knowing the constants a, b, c, . . ., s can be calculated.

2·3. Methods in Calorimetry.—The following are the chief methods[2] employed in Calorimetry[3] :—

1. Method of Mixtures.
2. Method of Cooling.
3. Methods based on Change of State or Latent Heat Calorimetry.
4. Electrical Methods.

In the following pages we shall discuss these methods one by one. Under every one of these we shall consider the various experimental arrangements that have been adopted. Solids and liquids will be considered first while gases will be taken up later in the chapter.

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[1] For historical references regarding specific heat see *The Discovery of Specific Heat and Latent Heats* (London, 1935) by Mckie and Heathcote.

[2] This classification is not very rigorous because sometimes there is an overlapping, and further, the fourth one is very general. We have adopted this grouping because it is convenient.

[3] A good account of these methods is given in Glazebrook, *A Dictionary of Applied Physics*, **1**, article on 'Calorimetry'.

1. METHOD OF MIXTURES

2·4. Theory of the Method.—Regnault about the year 1840 made a careful study of the Method of Mixtures, and by care and skill obtained results of the highest accuracy. The method consists in imparting the quantity of heat to be measured to a certain mass of water contained in a vessel of known thermal capacity and measuring the rise of temperature produced. Thus if a substance of mass m_1, specific heat s_1 and initial temperature θ_1, be plunged into m_2 grams of water at temperature θ_2 and if W be the thermal capacity of the calorimeter and θ the final temperature of the mixture, we have, by equating the heat lost by the substance to the heat gained by the water and calorimeter,

$$m_1 s_1 (\theta_1 - \theta) = (m_2 + W)(\theta - \theta_2),$$

or

$$s_1 = \frac{(m_2 + W)(\theta - \theta_2)}{m_1(\theta_1 - \theta)}.$$

This gives the specific heat of the substance. Various corrections are, however, necessary, for heat is lost by the system by conduction, convection and radiation. Thus for θ we must put $\theta + \triangle\theta$ where $\triangle\theta$ is the correction.

2·5. Radiation Correction.—In most experiments on calorimetry the calculation of this loss of heat due to radiation is important. The radiation correction may be calculated with fair accuracy with the aid of Newton's Law of Cooling (Chap. XV) which states that for small differences of temperature the heat loss due to radiation is proportional to the temperature difference between the calorimeter and the surroundings. To illustrate its application let AB (Fig. 1) denote the observed rise of temperature during an experiment, BC the observed cooling at the end of it. We have to calculate the true rise in temperature. Divide the abscissa into n intervals δt_1, δt_2, ... δt_n

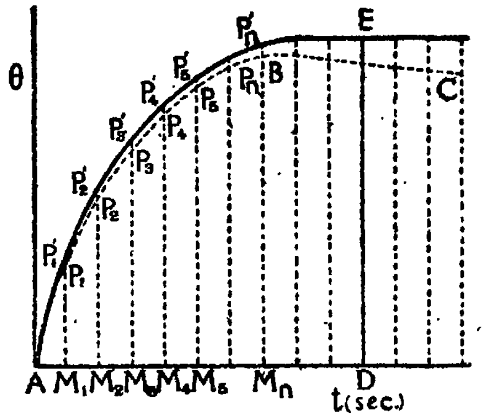

Fig. 1.—Illustration of Radiation Correction.

by means of ordinates P_1M_1, P_2M_2, ... P_nM_n such that the small portions AP_1, P_1P_2, ... $P_{n-1}P_n$, may be treated as straight lines. Let us measure temperatures from the temperature of the surroundings. If θ_1, θ_2........denote the mean temperatures during these intervals, θ_1', θ_2'........the temperatures at the ends of these intervals, represented by P_1M_1, P_2M_2........, then the temperature diminution due to radiation in the interval δt_1 is $k\theta_1\delta t_1$. If θ_1'', θ_2''........θ_n'' denote the temperatures at the ends of these intervals had there been no loss due to radiation, then

$$\theta_1'' = \theta_1' + k\theta_1\delta t_1 \quad \ldots \ldots \quad (3)$$

$$\theta_2'' = \theta_2' + k\theta_1\delta t_1 + k\theta_2\delta t_2 \quad \ldots \ldots \quad (4)$$

$$\therefore \quad \theta_n'' = \theta_n' + k\,(\theta_1\delta t_1 + \theta_2\delta t_2 + \ldots\ \theta_n\delta t_n)$$

$$= \theta_n' + k\ (\text{area of the curve } ABM_nA)$$

$$= \theta_n' + k\int_0^t \theta\, dt. \quad \ldots \ldots \quad (5)$$

We can thus correct any temperature θ_n' if we determine the area AP_nM_nA and k.

An alternative method is to plot the upper curve from the lower curve by increasing the ordinate M_1P_1 to M_1P_1', M_2P_2 to M_2P_2', etc., where $M_1P_1' = \theta_1''$, $M_2P_2' = \theta_2''$, etc. The highest ordinate on the curve (*viz.*, DE) gives the true rise of temperature in the experiment corrected for radiation.

To determine k we have to observe the rate of cooling at any temperature. The curve BC (Fig. 1) is obtained for this purpose experimentally. From this $d\theta/dt$ is calculated for any mean value θ. Now $k = -(1/\theta)d\theta/dt$ hence k is known.[1]

Another method known as the adiabatic method consists in completely preventing the heat loss from the calorimeter by enclosing the latter by a bath whose temperature is continuously adjusted and always kept equal to that prevailing in the calorimeter.

2·6. Specific Heat of Solids.—For finding the specific heat of solids by this method the requisites are a calorimeter with an enclosure, a thermometer and a heater. For work at ordinary temperatures the calorimeter is made of thin copper, nickel-plated and polished on the outside, so as to reduce radiation losses. It is supported on pointed pieces of wood or by means of thread inside a larger double-walled vessel which has water maintained at a fixed temperature in the annular space between the walls.

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[1] For other methods see Glazebrook, *A Dictionary of Applied Physics*, **1**, pp. 61-63.

The heater is a steam-jacket in which the substance is heated by steam without becoming wet. An oil bath may also be used. The transference and radiation errors must be reduced by suitable mechanical devices as in Regnault's classical experiments.

For high temperatures the solid substance is heated in an electric furnace. White[1] in his determination of the specific heat of silicates at high temperatures employed a furnace having a platinum coil wound on its interior surface. The substance was supported inside the furnace in a loop of platinum-wire and was allowed to drop into the calorimeter containing water by a suitable mechanical device. Change in temperature was measured by a resistance thermometer.

For work at low temperatures the substance is cooled down in a quartz vacuum-vessel[2] surrounded by liquid air before being dropped into the calorimeter.

Awbery and Ezer Griffiths[3] have determined the specific heat of solids and molten metals and salts as well as their latent heats of fusion by using an improved apparatus based on the method of mixtures. They took special precautions to prevent the loss of calorimetric liquid by evaporation. Their apparatus is described in Chap. XI.

The use of water as calorimetric liquid has several drawbacks. Its range is small and specific heat large so that the rise of temperature is small; further there is considerable risk of some water being lost by evaporation. For these reasons several workers have replaced it by a block of metal. The copper block calorimeter devised by Nernst, Lindemann and Koref[4] is exceedingly convenient for low temperatures. It consists of a heavy copper block K (Fig. 2) cemented with Wood's metal to the inside of a Dewar flask D. This block here plays the same part as water in the ordinary method of mixtures. The heated substance is dropped into the copper block through the glass tube R and the change in temperature of the block is read on thermocouples T, T one of whose ends is inside the copper block K and the other in the block C. The copper block on account of its good conductivity renders the temperature uniform throughout the mass in a short time.

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[1] *Phys. Rev.*, **31**, 670, 1910; *Amer. Jour. of Science*, **47**, 1919.

[2] Koref, *Ann. d. Physik*, **36**, 49, 1911; and see also Richards and Jackson, *Zeits. f. Phys. Chem.*, **70**, 414, 1910.

[3] *Proc. Phys. Soc. Lond.*, **38**, 378, 1926.

[4] *Ber. d. Pr. Akad. d. Wiss.*, **3** (Marz), 1910.

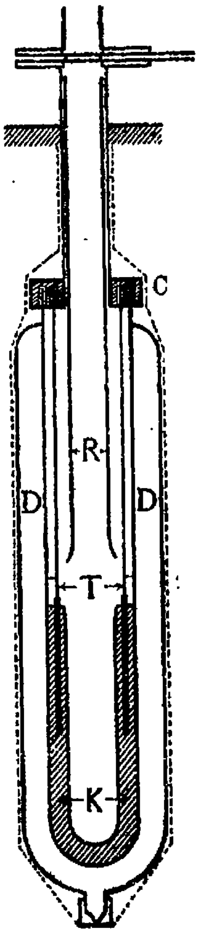

Fig. 2.—Copper Block Calorimeter.

This method has been employed by several recent workers for an accurate experimental determination of the specific heat of solids at high temperatures—a task which has acquired great importance in recent years on account of the unsatisfactory explanation offered by the present theories of specific heats of substances at high temperatures. Magnus[1] determined in this way the specific heat of platinum and other metals up to 900°C. The metal block calorimeter was also utilised, among others, by Hengstenberg,[2] Oberhoffer and Grosse[3] and Jaeger and his collaborators[4].

2·7. Experiments of Jaeger and Rosenbohm.—Jaeger and Rosenbohm determined the specific heats of W, Pt, Os, Rh, Ir, Ru and Pd upto about 1600°C and claim an accuracy of 0·1 per cent for their results. We shall describe their experiments in detail as they took very great care to eliminate all sources of error and obtained reliable and reproducible results.

Their calorimeter is indicated in Fig. 3. A is the aluminium block calorimeter of cylindrical shape. In its centre there is bored up to some depth a hollow cylindrical opening *a* to the lower part of which is fixed an aluminium piece provided with a steep conical boring *r*. The inside of the cylindrical cavity as well as that of the conical bore *r* is provided with a platinum lining. The heated object falls through the porcelain tube TT into the opening *a* and is first caught by a an extremely mobile trigger *n* which instantly closes the nickel lid Q. This mechanism thus works like a mouse-trap and prevents loss of heat by radiation from the substance. The temperature of the calorimeter is measured by 36 thermocouples of copper-constantan whose hot junctions are embedded in 36 narrow cylindrical borings (O,O......) arranged in two concentric circles and going down to 16 cm. depth. The thermocouples are connected in four series of nine each. The thermocouple leads pass through the wooden cover *cc* and their cold junctions are embedded into the borings of the copper ring N which is immersed in molten and subsequently resolidified paraffin P contained within the conical reservoir Y. The E. M. F. was measured with the help of a potentiometer free from thermo-electric contact potentials and P.D. smaller than the smallest decade unit were measured by the deflections of a calibrated galvanometer of 30 ohms resistance and having a sensibility of 10^{-10} amp. Thus it was possible, according to the authors, to determine temperature differences accurate to 0·0001°C. with absolute certainly.

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[1] *Ann. d. Physik*, **48**, 983, 1915; *Zeits. f. Physik*, **7**, 141, 1921.

[2] Hengstenberg, Dr. Ing. Dissertation, Breslau (1920); Bornemann and Hengstenberg, *Metall. u. Erz.*, **17**, 319, 339, 1920.

[3] *Stahl und Eisen*, **47**, 676, 1927.

[4] *Proc. K. Akad. Wet. Amst.*, **33**, 457, 1930; **30**, 905, 1927; **39**, 442, 912, 1936.

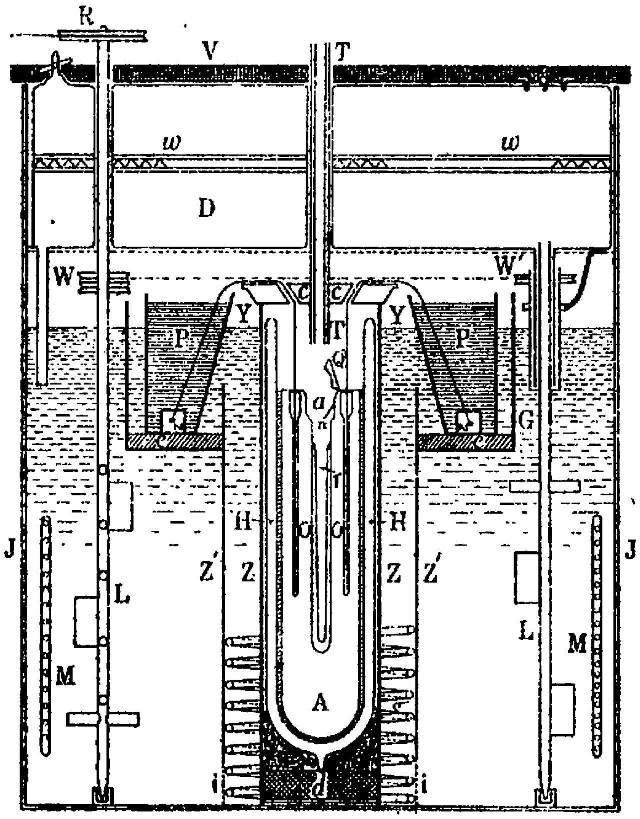

Fig. 3.—Calorimeter of Jaeger and Rosenbohm.

The aluminium block A fits tightly into a thin outer mantle of brass. The whole is placed inside the Dewar-vessel H of glass, the inside surface of which is coated with strips of aluminium foil of which a cushion is also made at the bottom. The Dewar-vessel is kept in position by being enclosed in a zinc cylinder Z containing a lead layer *d* at its bottom, and covered at its top with the wooden cover *cc*. Outside the cylinder Z there is another concentric zinc cylinder Z′ having holes *i*, *i* at the bottom and provided at the top with a wider copper mantle G having an ebonite base *e*. Z′ is surrounded by a much wider concentric cylinder J of zinc, nearly full of water and carefully insulated at the top with a water-bearing cover D and layer of felt V. The water in J is kept at a constant temperature to within 0·001°C. at about 20°C. with the help of three heating spirals M of nickelwire (one of which is connected to a special type of thermo-regulator) and the spiral tube *σ* just inside Z′ in which cold water is kept circulating. The water in J is kept vigorously stirred by three stirrers L, L worked by means of W, W′ and R, the last being set in motion by an electric motor. The water circulated through D and also in the space between Z, Z′. To diminish radiation, J is further surrounded by a double-walled wooden vessel containing slag wool.

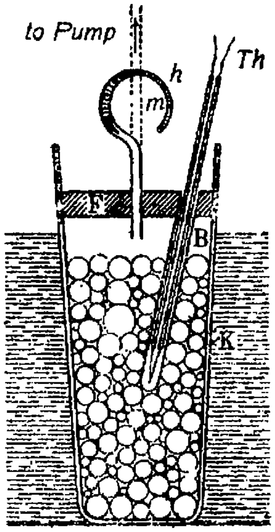

Fig. 4.—The experimental substance.

The experimental substance is first obtained in the form of globules and a known weight of these is placed inside the crucible K (Fig. 4) of iridium-free platinum. The shape of the crucible is such that it fits exactly within the conical opening *r* of the calorimeter A in figure 3.

The crucible is closed at the top with an exactly fitting cover F which has a tube B for inserting the Pt, Pt-Rh couple, and a platinum capillary *m* for connection to a vacuum pump. When the evacuation of the inside of the crucible is complete, the capillary *m* is drawn in the form of a loop *h* and closed.

The crucible K is suspended in the electrical furnace (shown in Fig. 5) by a thin platinum wire which can be melted by passing a strong electric current when the crucible is to be dropped into the calorimeter. The furnace EUI stands on the iron frame *f* which rests with three legs on the iron table *t* and the latter rests on *l* which can be moved on rollers. The furnace has a core S of hard magnesite having a platinum coil wound on its interior wall; outside S is a concentric cylinder of burnt magnesia and all these are enclosed by E, U and I which are made of chamotte. Radiation from the furnace to the room and the calorimeter is prevented by water jackets, shown in the figure, through which cold water circulates. The tube leading down from the furnace is just above T which, in turn, leads to the calorimeter but radiation of heat to the latter is prevented by

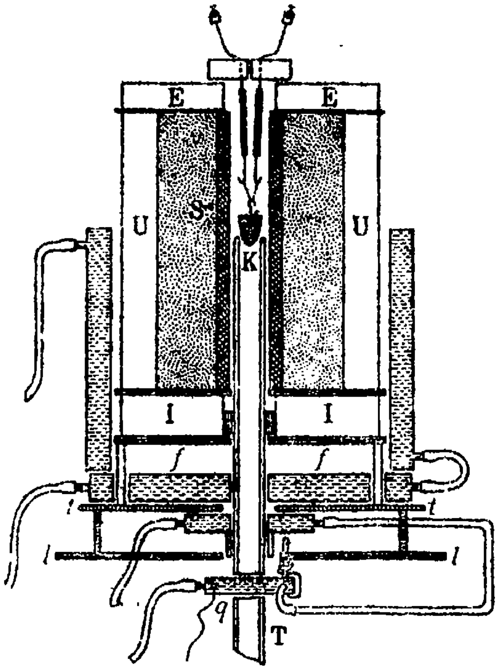

Fig. 5.—Furnace for heating the substance.

q which, however, can be removed for an instant when K falls into the calorimeter.

Experimental Procedure.—The water equivalent of the calorimeter was first found. For this purpose a known weight of water was put inside the platinum crucible and the latter heated to a known temperature and then dropped into the calorimeter. Knowing the specific heat of platinum, the thermal capacity of the calorimeter is easily calculated.

Next the experimental substance is enclosed in the crucible, kept in the furnace for an hour and then dropped into the calorimeter. From the rise in the temperature of the latter the total heat given by the crucible in falling to 20°C. is known, and subtracting the contribution of the crucible, the heat given by the substance is found. Knowing the specific heat of the substance in the range 0—20°C. the amount of heat Q that would be given by the substance in cooling from t° to 0°C. is calculated. From such measurements for different temperatures t, the quantity Q or the mean specific heat $\bar{s}$ between 0 and t° can be represented as a function of t. From this the true specific heat of the substance at any temperature can be calculated as explained on page 50.

2·8. Specific Heat of Liquids.

—Specific heat of liquids which do not react chemically with water or any other substance of known specific heat may be obtained by direct mixture. For liquids which react in this way Regnault used a different form of apparatus. The liquid was not allowed to mix with water but was admitted when desired into a vessel immersed in water. The liquid was first heated and then forced into the vessel. The specific heat could be calculated as before.

Another class of experiments for measuring the specific heat of liquids involves the expenditure of some mechanical energy and measurement of the consequent rise of temperature. To this class belong the classical experiments of Rowland for determining the mechanical equivalent of heat. They will be described in detail in Chapter III.

A very ingenious modification of the method of mixtures has been devised by Callendar[1] which is known as the *Continuous-mixture method.* In this the same current of water first flows as a hot current and then after being further cooled, it flows as a cold current exchanging heat with the hot current in a suitable exchanger. Thus the mean specific heat of the hot water could be directly compared with the mean specific heat of the cold water.

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[1] *Phil. Trans., A,* **212,** 1, 1912.

2. METHOD OF COOLING

2·9 This method, perfected by Dulong and Petit, is found to be most convenient for liquids but unsuitable for solids owing to variations of temperature within the latter. The method is based on the assumption that when a body cools in a given enclosure on account of radiation alone, the heat δQ emitted in the time dt is given by the relation

$$\delta Q = Af(\theta)\,dt, \quad . \quad . \quad . \quad . \qquad (6)$$

where A depends upon the area and the radiating power of the surface and $f(\theta)$ is an unknown function of θ, the excess of the temperature of the body over that of the surroundings. If this produces a cooling of the body through $-d\theta$, then

$$\delta Q = -ms\,d\theta. \quad . \quad . \quad . \quad . \qquad (7)$$

Combining this with (6), we get

$$-ms\,d\theta = A\,f(\theta)\,dt.$$

Or
$$\int_0^t dt = -\frac{ms}{A}\int_{\theta_1}^{\theta_2}\frac{d\theta}{f(\theta)}.$$

Or
$$t = \frac{ms}{A}\int_{\theta_2}^{\theta_1}\frac{d\theta}{f(\theta)}. \quad . \quad . \quad . \quad . \qquad (8)$$

Similarly for another substance to cool through the same interval of temperature

$$t' = \frac{m's'}{A'}\int_{\theta_2}^{\theta_1}\frac{d\theta}{f(\theta)}. \quad . \quad . \quad . \quad . \qquad (9)$$

If $A=A'$, *i.e.*, the surface area and the radiating power of the two bodies be the same, we have from (8) and (9)

$$\frac{ms}{t} = \frac{m's'}{t'}. \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

If masses m, m' of two liquids be contained successively in a calorimeter of thermal capacity W and the calorimeter suspended inside a vessel kept at 0°C. by immersion in melting ice, and then observations of the rate of cooling taken, we have

$$\frac{W+ms}{t} = \frac{W+m's'}{t'}. \quad . \quad . \quad . \quad . \qquad (11)$$

If one liquid is water ($s=1$), the specific heat of the other is thus determined from a knowledge of t, t', m, m'.

The method[1] is sometimes employed for determining the specific heat of liquids but is not capable of any great accuracy and is mainly of historical interest. It has, however, been adopted by Marley[2] to the determination of the specific heat of poor conductors.

3. METHODS BASED ON CHANGE OF STATE

2·10. The heat to be measured may be applied to a solid at its melting point or to a liquid at its boiling point and the corresponding amounts of liquid or vapour thereby produced may be measured. This gives rise to two methods. These methods were of real advantage in the last century when accurate measurements of temperature were not possible, but with the recent development of accurate thermometers and electrical heaters, they are now less in use, chiefly on account of their inherent defects. We may also employ the converse process, *viz.*, we may use the vapour to heat a substance so that a part of it becomes condensed, and measure the amount condensed. This is employed in Joly's steam calorimeter which is very convenient for determining the specific heat of gases at constant volume.

2·11. Method of Melting Ice.—In this method the heat given out by a certain substance in cooling is imparted to ice and measured by the amount of ice thereby melted. Thus if M grams of a substance of specific heat s and initial temperature θ are able to melt m grams of ice when placed in contact with the latter, the specific heat is given by the relation

$$Ms\theta = mL, \qquad . \quad . \quad . \quad . \qquad (12)$$

where L is the latent heat of fusion. An improved form of the apparatus devised by Bunsen will now be described.

2·12. Bunsen's Ice Calorimeter.—In this calorimeter the water produced by the melting of ice is not drained off but is allowed to remain mixed with ice and the resulting change in volume observed. The calorimeter is illustrated in Fig. 6. The test-tube A is fused into the cylindrical glass bulb B which is provided with the glass stem C. B is nearly filled with boiled air-free water and the remaining space and the stem is filled with mercury. The stem terminates in an iron-collar D containing mercury into which a graduated capillary tube E is pushed so that mercury stands at a certain graduation in E.

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[1] For a new application of the cooling method by Saladin, see *Handbuch der Experimental-physik*, Vol. **8**, p. 152.

[2] *Proc. Roy. Soc. Lond.*, **45**, 591, 1933.

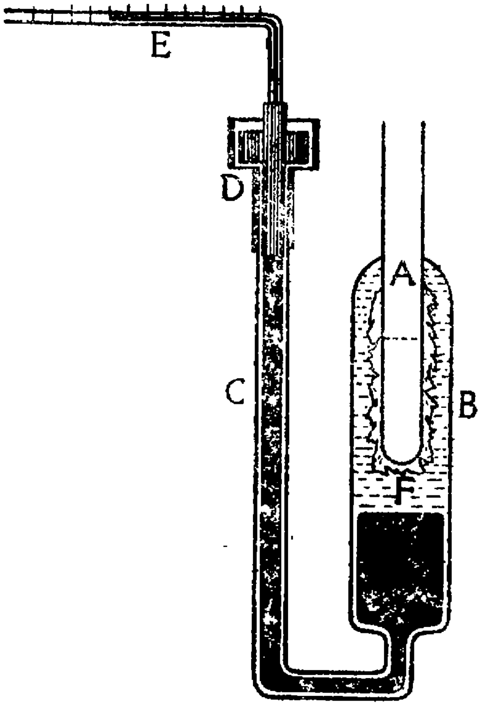

Fig. 6.—Bunsen's Ice Calorimeter.

In conducting an experiment, a stream of alcohol cooled by a freezing mixture, is first passed through the test-tube A until a cap of the ice F is formed round it in B. The whole instrument is then kept immersed in pure ice at 0°C. for several days till all the water in B is frozen. It is then ready for use.

To calibrate the scale on E, let a mass m of water at a temperature θ°C. be poured into the test-tube A. Some ice in B melts and the resulting contraction of mercury, say, n divisions on E is observed. Then if a recession of mercury by 1 division corresponds to q calories of heat

$$m\theta = nq, \text{ or } q = m\theta/n. \quad . \quad . \quad . \quad . \quad (13)$$

Next the substance under investigation, previously heated to a temperature θ' is dropped into some water at 0° contained in the test-tube A. Then if M, s denote the mass and the specific heat of the substance respectively, and n' the observed recession of mercury thread in E, we have

$$Ms\theta' = n'q,$$

or

$$s = \frac{n'}{M\theta'}q = \frac{mn'}{Mn}\frac{\theta}{\theta'}. \quad . \quad . \quad . \quad . \quad (14)$$

This gives the specific heat of the substance. The specific heat of the metals which can be had in small quantities can be readily found by this method.

The accuracy attained by this apparatus is, however, limited. The ice in the surrounding vessel may not be at the same temperature as that in the vessel B, thus a progressive heating or cooling of ice in B may take place. A serious objection to the use of the ice-calorimeter, however, rests on the fact that a given specimen of water can freeze into ice of different densities.

2·13. Joly's Steam Calorimeter.—In the steam calorimeter devised by Prof. Joly[1] in 1886 the heat necessary to raise the temperature of a substance from the ordinary temperature to the temperature of steam is measured by the amount of vapour condensed into water at the same temperature. It consists of a thin metal enclosure A (Fig. 7), double-walled and covered with cloth, which is placed beneath a sensitive balance. One pan of the balance is removed and from this end of the beam hangs freely a wire *w* supporting a platinum pan P inside the enclosure. The substance whose specific heat is required is placed on this pan and weights added on the other pan till balance is attained. The temperature of the enclosure is observed by means of a thermometer inserted into the chamber, and in the meantime steam is got up in the boiler. It is then admitted suddenly into the chamber through the wide opening O at the top and can escape through the narrow exit-tube *t* at the bottom. Steam condenses on the substance and the pan, and weights are added on the other pan to maintain the equilibrium. When the pan ceases to increase in weight the readings are noted and the temperature of the steam read on a thermometer. During the final weighing the steam is

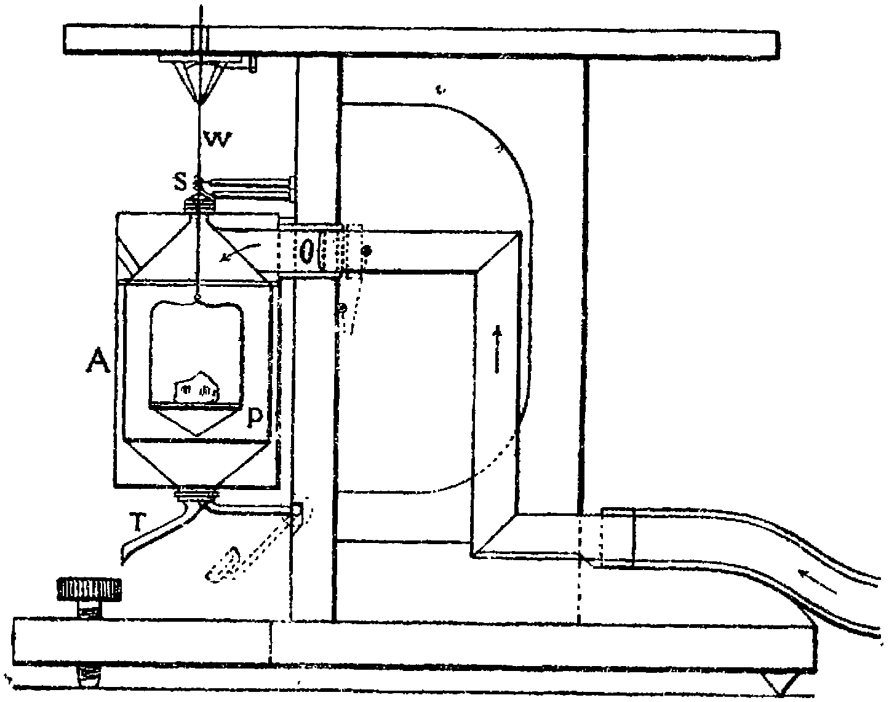

Fig. 7.—Joly's Steam Calorimeter.

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[1] *Proc. Roy. Soc. Lond.*, **41**, 352, 1886.

allowed to enter the chamber through a narrow escape-tube so as not to disturb the pan. The weight becomes practically constant in four or five minutes though a very slow increase of about 4 milligrams per hour due to radiation may be observed. The difference between the two weighings gives the weight of steam condensed.

Let M be the weight of the substance, w, the increase in weight of the pan, θ_1, the initial temperature of the enclosure, θ_2, the temperature of steam, W, the thermal capacity of the pan, L, the latent heat of steam, s, the required specific heat, then

$$Ms(\theta_2 - \theta_1) + W(\theta_2 - \theta_1) = wL. \quad (15)$$

W is determined from a preliminary experiment without any substance on the pan and thus the specific heat of the substance is found.

For great accuracy various precautions and corrections are necessary. Steam condenses on the suspending wire where it leaves the chamber and then surface tension renders accurate weighing difficult. A thin spiral s of platinum wire in which a current flows usually surrounds the suspending wire just above the opening, and is made to glow so that the heat developed is just sufficient to prevent condensation. A rapid introduction of steam is necessary in the early stages, for steam also condenses on the pan due to radiation to the cold air and the chamber, thus causing error. This is of course partially balanced by radiation from the steam to the substance later. Further, w does not accurately represent the weight of steam condensed since the first weight is taken in air at θ_1°C. and the second in steam at θ_2°C. All the weighings must be reduced to vacuum and then the increase in weight calculated. Specific heat of rare substances can be found by this method since small quantities of the substance are needed but a sensitive balance is indispensable. The specific heat of liquids and powders can be found by enclosing them in glass or metal spheres whose thermal capacity is taken into account. Gases can also be similarly enclosed, but then the modified form of the apparatus—the differential calorimeter is used.

In the *differential steam calorimeter* invented by Joly[1] in 1889, both the balance pans are made exactly similar and of equal thermal capacity and hang in the same steam-chamber (Fig. 8). The substance to be tested is placed on one pan and the excess of steam condensing on this pan over that on the other pan is entirely due to the substance. Thermal capacity of the pans, radiation from them and all other sources of error common to them are eliminated, the substance bearing only its own share of the error. The chief use of this apparatus, however, consists in the determination of the specific heat of gases at constant volume. The pans are then replaced by two equal hollow spheres of copper furnished with "catchwaters" (shown in the figure). One sphere is filled with the dried experimental gas at any desired pressure while the other is empty. They are counterpoised by adding necessary weights m which represent the mass of the contained gas. Steam is admitted and condenses on the pans. Greater steam condenses on the sphere containing the gas, the excess, say, w giving the steam required by the gas. Now the specific heat at constant volume c_v may be calculated from the equation

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[1] *Proc. Roy. Soc. Lond.*, **47**, 218, 1889.

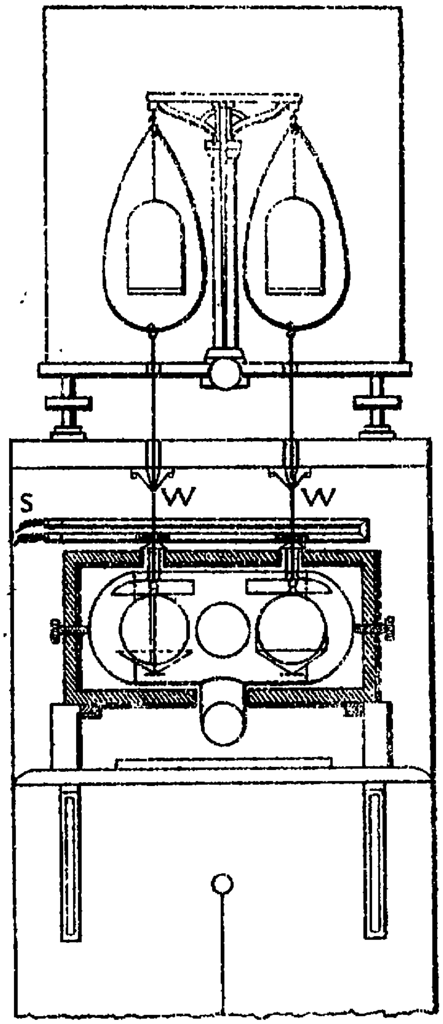

Fig. 8.—The differential Steam Calorimeter.

$$mc_v\,(\theta_2-\theta_1) = wL, \qquad (16)$$

where θ_2, θ_1 are the final and initial temperatures of the chamber.

Joly used copper spheres of diameter 6·7 cm. and weighing 92·2 gm. and employed gases at different pressures. Corrections were applied for the following :—

1. The expansion of the sphere due to increased temperature and the consequent work done by the gas in expanding to this volume.
2. The expansion of the sphere due to the increased pressure of the gas at the higher temperature.
3. The thermal effect of this stretching of the material of which the sphere is made.
4. The increased buoyancy of the sphere due to its increased volume at the higher temperature.
5. The unequal thermal capacities of the spheres.

6. The reduction of the weight of water condensed to its weight in vacuum.

The steam calorimeter has been employed by Carlton-Sutton[1] to measure the latent heat of steam directly in terms of the mean calorie. A bulb, first empty and next filled with water at 0°C., was heated by the steam from 0 to 100°C. From the mass of steam condensed in the two cases and knowing other constants, the mean specific heat of water between 0° and 100°C. could be calculated.

2·14. Vaporisation Calorimeters.—Dewar[2] devised calorimeters based on an analogous principle in which he employed a liquefied gas as the calorimetric substance. The heat to be measured is applied to the liquefied gas whereby the liquid evaporates absorbing its latent heat and the volume V of gas thus produced is measured. The heat communicated to the liquid is then given by $V\rho L$ where ρ is the density of the vapour and L the latent heat of vaporisation of the substance. Using liquid oxygen and liquid hydrogen the apparatus can be adopted for very low temperatures. In case of hydrogen 1 c. c. of vapour at N.T.P. corresponds to a very small quantity of heat (about 1/100 calorie) and consequently vapour calorimeters have been used by Curie and Dewar[3] for measuring the heat of formation of radioactive products.

This method has been utilised for measuring the specific heat down to very low temperatures. The experimental substance (solid or liquid) is first kept in a constant temperature bath (say 0°C.) and then dropped into the calorimeter containing liquid O_2 or H_2.

4. ELECTRICAL METHODS

The electrical method was first employed by Joule in his attempts to determine the mechanical equivalent of heat. The electrical methods at present available may be sub-divided into two :

1. Methods based on the observation of rise of temperature.
2. Method employing the steady-flow electric calorimeter.

We shall first consider the application of these methods to liquids because historically the method was first applied to them.

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[1] *Proc. Roy. Soc. Lond.*, **93**, 155, 1917.

[2] *Proc. Roy. Soc.*, *A*, **76**, 325, 1905, **89**, 158, 1913; see also Dewar, 'Collected Papers,' Cambridge (1927), p. 1399.

[3] *Proc. Roy. Inst.*, **17**, 581, 1904; Curie, *Radioaktivität*. See Taylor and Rinkenbach, *Jour. Amer. Chem. Soc.*, **64**, 1505, 1924; Dewar, *loc. cit.*

2·15. Methods Based on the Rise of Temperature.—Following Joule this method was adopted by many workers. Griffiths,[1] Schuster and Gannon, W. R. and W. E. Bousfield[2], and Jaeger and Steinwehr[3] employed this method for determining the mechanical equivalent of heat and found that it was capable of the highest accuracy. The same arrangement[4] may be employed for finding the specific heat of liquids. The foregoing workers used only water, but other workers used other liquids. Babcock[5] measured the specific heat of liquid ammonia at high temperatures. An adiabatic form of apparatus was used by Trehin[6] and Cohen and Moseveld.[7]

The principle of the method is to generate heat by passing a current through a conductor. If i is the current through a conductor of resistance R and E the potential difference across its ends, the energy spent in a time t seconds is Eit ergs provided E and i are expressed in electromagnetic units. If this raises the temperature of M grams of a substance by $\delta\theta$, the specific heat s of the substance is given by the relation

$$Eit=JMs\,\delta\theta, \qquad (17)$$

where J is the mechanical equivalent of heat (see Chap. III). If E is expressed in volts and i in amperes, the energy spent is given in Joules.

Any two of the quantities E, i, and R may be measured thus giving three methods. Griffiths, in his determination of the specific heat of water, chose to measure E and R which is rather difficult for R must be measured during the heating experiment. Griffiths' work is important since it first established the fact that the electrical method can accurately give the value of J in absolute units.

2·16. Experiments of Jaeger and Steinwehr.—Jaeger and Steinwehr applied this method to determine the mechanical equivalent of heat and hence also the specific heat of water at temperatures between 5° and 50°C. They carried out the experiments very carefully and aimed at an accuracy of 1 in 10,000. Their results are very reliable and, therefore, we shall describe their experiment in some detail.

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[1] *Phil. Trans.*, *A* (1893); *Proc. Roy. Soc.*, **55**, 1894.

[2] *Phil. Trans.*, *A*, **211**, 236, 1911.

[3] *Ann. d. Physik*, **64**, 305, 1921.

[4] A detailed account of these methods will be found in Glazebrook, *A Dictionary of Applied Physics*, **1**, pp. 485-490 (1922 edition).

[5] *Proc. Amer. Acad.*, **55**, 325, 1920.

[6] *Ann. Chim. Phys.* (9), **15**, 246, 1921.

[7] *Zeits. f. phys. Chem.*, **95**, 305, 1920.

They employed a large mass of water (50 Kgm.) and consequently the thermal capacity of the vessel was only a small fraction (about 1%) of that of the contained water. This also made the loss of heat by radiation from the surface small in comparison with the electrical energy supplied. The mass of water, though very large, was measured accurately on a special equal-armed balance. The rise in temperature produced by the electrical energy was kept small (about 1·4°C.) with the specfic object that Newton's law of cooling should hold accurately throughout the interval. This is, however, of doubtful utility as the departure from Newton's law would be hardly appreciable while the small rise makes accurate measurements of temperature extremely difficult.

A section of their apparatus is shown in Fig. 9. AA is the cylindrical copper calorimeter lying on its side on procelain insulators and is thereby insulated from the surrounding constant-temperature bath B. On the upper side at O there is a hole for the introduction of the heating coil H, the resistance thermometer and the shaft *t* which drives the stirrer SS. The hole can be closed by a lid through which the respective leads pass and are soldered. The stirrer is rotated at a constant rate of about one revolution in two seconds and the energy developed by it which was about one watt, was found.

The heating coil of constantan wire was 1 mm. in diameter and 14 m. long and had a resistance of about 8 ohms. It was covered with silk and shellacked, and wound on a brass cylinder. Upon this another brass cover was placed and properly soldered. The wire was heated by a current of about 10 amp. The strength of the current was accurately measured by including a standard 0·1 ohm coil in series and measuring the P. D. across it on a carefully calibrated potentiometer. The P. D. across the heater was similarly measured by permanently keeping a resistance of 10,000 + 127 ohms in parallel with the heater and measuring the P. D. across the 127 ohm resistance. The time for which the current flowed was about 6 minutes and was recorded automatically on a chronograph. The electrical energy supplied was about 800 watts.

The calorimeter was surrounded by a double-walled metal box B the space between the walls being full of water in which was kept immersed a long coil through which water at a regulated temperature could be passed. Thus the temperature of the surrounding bath could be kept constant at any desired value and the radiation loss from the calorimeter was kept small and regular. This was corrected for by observing the rate of cooling before and after the experiment the temperature was measured by a carefully calibrated platinum thermometer. The small temperature rise necessitated resistance measurements accurate to [1] in 2 millions in order that temperature measurements be accurate to 1 in 10,000. This was hardly possible and hence the individual results obtained by these investigators show departure by a few hundredths of a per cent.

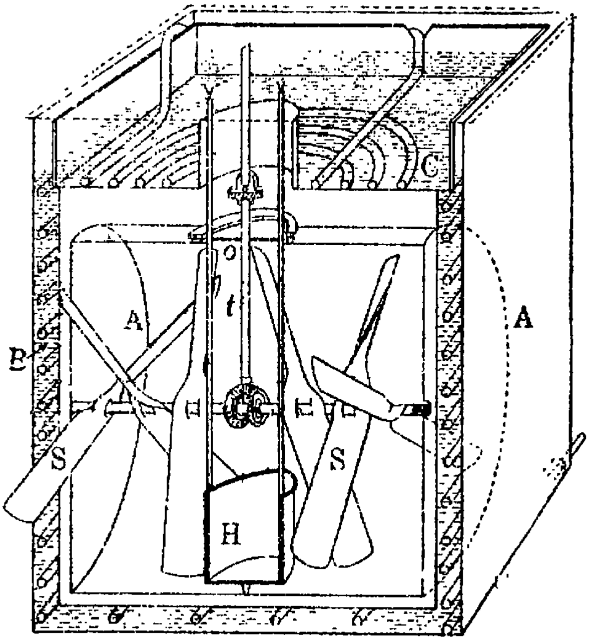

Fig. 9.—A section of Jaeger and Steinwehr's Calorimeter.

2·17. Experiments of Osborne, Stimson and Ginnings.—A very accurate determination of the mechanical equivalent of heat and hence also of the specific heat of water by the electrical method has been carried out by Osborne, Stimson and Ginnings[1]. Their calorimeter contained water, which was partly in the liquid and partly in the vapour state. The water was obtained free from dissolved gases by distilling and then redistilling under reduced pressure. It was heated by an electrical heater immersed in the water and the rise of temperature measured by platinum thermometer. The temperature of the surroundings of the calorimeter was controlled and adjusted to be nearly the same as that of the calorimeter itself. In this way the specific heat and heat of vaporization of water, the enthalpy of water, the enthalpy and specific volume of water vapour were all determined from the ice point to the steam point.

2·18. The Method of Steady-flow Electric Calorimeter.—Great accuracy has been attained by Callendar and Barnes[2] by using the steady-flow electric calorimeter shown in Fig. 10. A steady current of the experimental liquid flowing through the narrow glass-tube *t*, about 2 mm. in diameter, is heated by an electric current flowing through the central conductor of platinum. The steady difference of temperature $\delta\theta$ between the inflowing and outflowing water is measured by a pair of platinum thermometers *Pt* at each end connected differentially in the opposite arms of a bridge of Callendar and Griffiths' type. The bulb of each thermometer is surrounded by a thick copper tube of negligible resistance attached to the central conductor. This on account of its good conductivity keeps the bulb uniformly at the temperature of the adjacent water, and due to its low resistance prevents generation of any appreciable amount of heat by the current close to the thermometer. The leads L, L and P, P are attached to this tube of copper, the former for introducing the heating current and the latter for measuring the potential difference across the central conductor in terms of a standard Clark cell by means of an accurately calibrated potentiometer. The potentiometer also serves to measure the heating current *i* from the value of the potential difference across a standard resistance included in the same circuit. In order to diminish the external loss of heat the flow tube is enclosed in a hermetically sealed glass vacuum-jacket surrounded by a constant-temperature water jacket whose temperature was kept constant by a delicate electric regulator.

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[1] *Bur. of Stand. J. of Research,* **23**, 197, 1939.

[2] *Phil. Trans.*, A, **199**, 55, 1902.

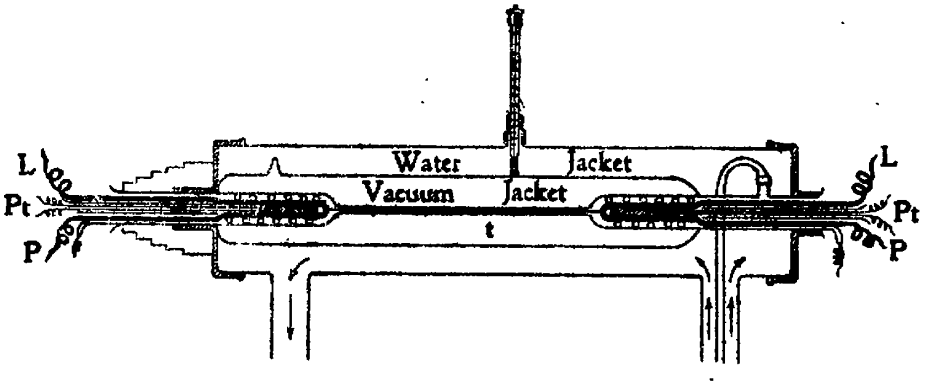

Fig. 10.—Steady-flow Electric Calorimeter.

Neglecting small corrections the general equation is

$$Eit = JMs(\theta_2 - \theta_1) + Jht, \quad . \quad . \quad . \quad (18)$$

employing the same notation as before, where *h* denotes the heat loss per second on account of radiation, and θ_1, θ_2, the temperatures of the inflowing and outflowing water respectively. The time of flow t in these experiments was about 20 minutes and was recorded automatically on an electric chronograph reading to 0·01 sec. The mass of water M was measured by collecting the outflowing water and was about 500 gm. The difference in temperature $\theta_2-\theta_1$ was from 8° to 10°C. and was accurately read to ·001°C. The heat loss h was very small and regular, and was determined and eliminated by suitably adjusting the electric current so as to secure the same rise of temperature for different rates of flow of the liquid. Thus for two rates of flow we have

$$E_1 i_1 t = JM_1 s\,(\theta_2-\theta_1)+Jht,$$

$$E_2 i_2 t = JM_2 s\,(\theta_2-\theta_1)+Jht.$$

$$\therefore J = \frac{(E_1 i_1 - E_2 i_2)\,t}{(M_1-M_2)\,(\theta_2-\theta_1)s}.$$

Since the temperatures at every point of the apparatus are the same in both experiments the heat loss h must also be the same. The specific heat s thus determined is the average specific heat for the interval $\theta_2-\theta_1$ and may be taken as the specific heat at the middle of the interval.

The great advantage of this steady-flow electric method is that no correction is necessary for the thermal capacity of the calorimeter since there is no change of temperature in any part of the instrument. Care must, however, be taken to secure perfect steadiness as it is practically impossible to correct for unsteady conditions. Further, since all conditions are steady, the observations can be taken with the highest degree of accuracy. There is no question of thermometric lag. It is essential, however, that the current of water be thoroughly mixed otherwise temperature over a cross-section of the tube will not be uniform; this is secured by having the central conductor in the form of a spiral instead of a straight wire.

Callendar and Barnes used this method to find the specific heat of water at various temperatures. Their results are discussed in the next article. Callendar[1] found the specific heat of mercury with this apparatus. The central conducting wire was dispensed with, the flowing mercury itself serving as the conductor. Griffiths[2] employed this method to determine the specific heat of aniline over the range 15° to 50°C. Burnett and Roebuck[3] have used a modified form of the apparatus in which the liquid was made to flow radially across the heating coils, these latter being wound between two porous tubes.

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[1] *Phil. Trans.*, *A*, **199**, 104, 1902.

[2] *Phil. Mag.*, 1895. *Proc. Camb. Phil. Soc.*, 1895, **8**, Part, 4.

[3] *Phys. Rev.*, **30**, 529, 1910.

2·19. Specific Heat of Water.—In ordinary calorimetric experiments the specific heat of water is assumed constant at all temperatures and equal to unity. Accurate investigations of the last article, however, show that it varies with temperature. The first accurate experiments for determining this variation of the specific heat of water are those of Rowland[1] in connection with his determination of the mechanical equivalent of heat (Chap. III). He argued that if the specific heat of water at all temperatures were constant this mechanical equivalent must come out a constant quantity even if we used water at different temperatures. The variation in the value of J was due to the variation in specific heat.

The other accurate experiments on the subject are those of Callendar and Barnes (sec. 2·18) and of Jaeger and Steinwehr (sec. 2·16). Both of them determined accurately the specific heat of water at various temperatures. Their values are given in Table 1 together with the values obtained recently by Osborne,

Table 1.—*Specific Heat of Water at different temperatures in int. Joules/gm.*

Temp. °C.	Specific heat (Barnes[2])	Specific heat (J & S)	Specific heat (O, S & G)	Temp. °C.	Specific heat (Barnes[2])	Specific heat (O, S &G)
0	..	..	4·2169	55	4·1749	4·1816
5	4·2035	4·1966	4·2014	60	4·1775	4·1836
10	4·1909	4·1897	4·1914	65	4·1800	4·1860
15	4·1825	4·1842	4·1850	70	4·1828	4·1888
20	4·1768	4·1800	4·1811	75	4·1855	4·1920
25	4·1731	4·1771	4·1788	80	4·1884	4·1956
30	4·1710	4·1755	4·1777	85	4·1912	4·1997
35	4·1703	4·1753	4·1774	90	4·1940	4·2043
40	4.1703	4·1764	4·1778	95	4·1968	4·2095
45	4.1712	4·1788	4·1787	100	..	4·2152
50	4·1728	4·1826	4·1799	..	..	..

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[1] *Proc. Amer. Acad. of Arts and Sciences*, 7, 1879-80.

[2] See *Phil. Trans.*, **212**, 30, 1913.

Stimson and Ginnings[1] at the National Bureau of Standards, Washington. The specific heat is expressed in international Joules[2] per gram per °C.

The values given in the second column have been recalculated from Barnes' results for the sake of comparison. The results of all these three investigations are plotted in Fig. 11. It will be seen that the values obtained by Callendar and Barnes lie somewhat wide of the others and appear to be less reliable chiefly on account of the uncertainty in the values of the electrical units employed. From these curves it is evident that water has a minimum specific heat at about 34°C.

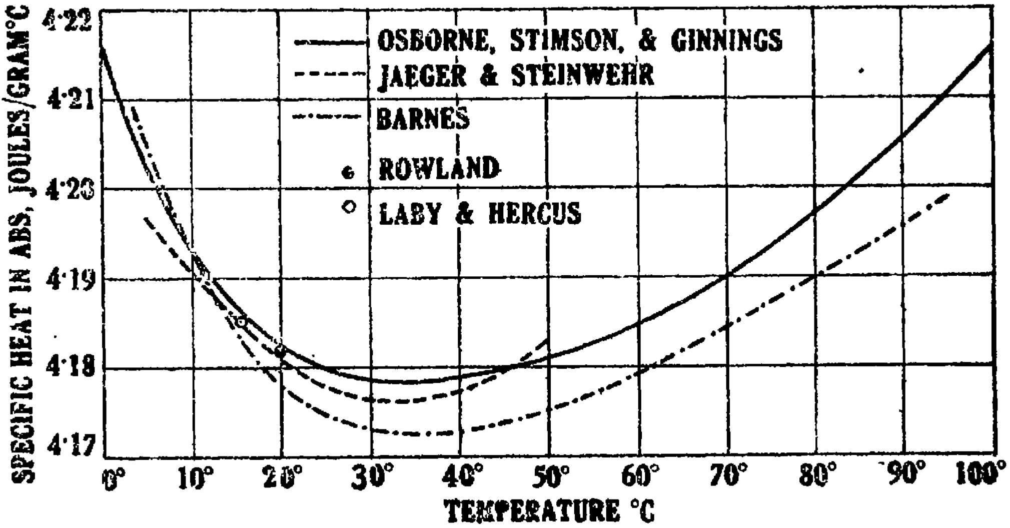

Fig. 11.—Specific heat curve for water.

Specific Heat of Solids

2·20. Rise of Temperature Method.—The electrical method was first applied to solids by Gaede[3] in 1902. E. H. Griffiths and E. Griffiths[4] determined the specific heat of many metals over the range −160° to +100°C. The substance was used in the form of a calorimeter and was first cooled below the desired temperature. Electrical energy was utilised in heating the calorimeter and the temperature indicated by a resistance thermometer. The calorimeter was enclosed in a constant temperature bath whose temperature was kept constant to 1/100th of a degree by cooling the vessel with the aid of a spiral tube through which previously cooled air was allowed to flow at a regulated rate. Correction was applied for the heat lost by radiation.

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[1] *Bur. of Stand. J. of Research*, **23**, 197, 1939.

[2] 1 int. Joule $= 1{\cdot}00041 \pm 0{\cdot}00010$ abs. Joule $= 1{\cdot}00041 \times 10^7$ ergs.

[3] *Phys. Zeits.*, **4**, 805, 1902.

[4] *Phil. Trans.*, *A*, **213**, 1913. *Proc. Roy. Soc.*, *A*, **89**, 561, 1914.

This method has been utilised by Dickinson and Osborne[1], Pirani (1912), Perrier and Roux[2], and others particularly for the measurement of specific heat at high temperatures.

2·21. Nernst Vacuum Calorimeter.—A different form of the apparatus, known as the *vacuum calorimeter*, was used by Nernst and Lindemann[3] for measuring specific heat at very low temperatures. This differed from the foregoing ones essentially in having the calorimeter suspended in *vacuum*. The results achieved with its aid are of great theoretical importance and hence their apparatus will be considered in some detail. For good conducting solids, such as metals, the calorimeter shown in Fig. 12 (a) was used. The substance whose specific heat is to be determined is shaped into a cylinder C, having a cylindrical hole drilled almost through its entire length, and a closely fitting plug P made for it from the

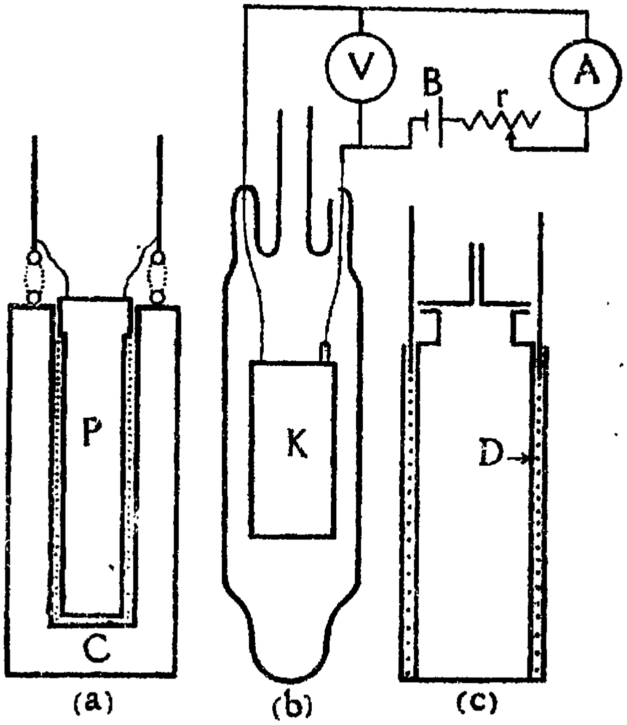

Fig. 12.—Nernst Vacuum Calorimeter.

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[1] *Bull. Bur. Stand.*, **12**, 23, 1915.

[2] *Mem. de la Soc. Vaud.*, **3**, 109, 1923.

[3] *Journal de Physique*, [4] **9**, 1910 ; *Ann. d. Physik*, **36**, 395, 1911.

same material. The substance here acts as its own calorimeter. The plug is wound over with a spiral wire of purest platinum (shown dotted in the figure) which is insulated from it by means of thin paraffined paper and finally liquid paraffin is poured over it. The upper part of the plug is somewhat thicker than the lower part, thus a good thermal contact is obtained. The calorimeter K thus constructed is suspended inside a pear-shaped glass bulb [shown at (b)] which can be filled with any gas or evacuated. The whole can be surrounded by suitable low temperature baths, such as liquid air or liquid hydrogen. The platinum spiral, which serves both as electric heater and resistance thermometer, is connected in series with the battery B, resistance r and a precision ammeter A, the voltmeter V indicating the potential difference across the spiral.

To carry out an experiment, the calorimeter was first brought to the desired temperature by introducing hydrogen, which is a comparatively good conductor of heat, into the pear-shaped vessel and then surrounding the latter by a suitable bath. Then the vessel was completely evacuated and surrounded by a low temperature bath, so that the loss of heat by radiation was small and regular and could be taken into account while the loss due to conduction and convection was entirely eliminated. A current was then allowed to flow through the heater for t seconds and the voltage across it was adjusted to be constant by varying the resistance r. If R_f, R_i, and i_f, i_i denote the final and initial values of the resistance of the heater and the current through it respectively, and E the constant potential difference,

$$R_f = \frac{E}{i_f}; \; R_i = \frac{E}{i_i}. \qquad (19)$$

Thus an observation of i_f, i_i, and E gives R_f and R_i, and from a previous determination of the resistance of the platinum spiral at various temperatures the rise in temperature $\delta\theta$ can be found. The energy supplied electrically is Eit where i is the average value of the current. Now if M is the mass of the substance forming the calorimeter, s its specific heat, we have

$$Eit = JMs\delta\theta + h. \qquad (20)$$

This gives the specific heat at a single temperature since $\delta\theta$ is usually 1 or 2°. The heat capacity of the paper and paraffin is very small and can be found and eliminated by taking different amounts of the experimental substance and at the same time arranging that the temperature rise is the same. The heat loss *h* is very small and regular and is determined and accounted[1] for by observing the rate of cooling before and after the experiment. Further, small corrections have to be applied for the fall of P.D. across the ammeter, the current through the voltmeter and the energy spent in the connecting leads to the heater.

For *non-conducting* solids the calorimeter shown in Fig. 12(c) was employed. The heating wire was wound over a cylindrical silver vessel D and the whole covered with silver foil to diminish heat loss. This foil was soldered at the bottom of the cylinder as indicated. The solid whose specific heat is required was placed inside the silver cylinder and the latter closed with the lid. The silver on account of its high conductivity keeps the temperature uniform and this is further secured by filling the cylinder with air through the tube in the lid. The tube is then closed with a drop of solder so that it may be gas-tight. It is absolutely necessary that air should be present inside the vessel to facilitate equalisation of temperature throughout the experimental substance. The heat capacity of the silver vessel was calculated and also determined experimentally. Liquids and gases can be similarly admitted into the cylinder and their specific heat determined.

In this method very accurate measurement of temperature is necessary since the rise of temperature is only 1 or 2°. For work at very low temperatures the platinum wire was calibrated by comparing it throughout the range with a lead resistance thermometer (see p. 37). But this does not completely solve the difficulty for at these low temperatures the resistance of the platinum wire changes considerably owing to the introduction of the electrical energy. Consequently Eucken and Schwers[2] in their work used a constantan wire as the heater and a lead wire as the resistance thermometer. These considerations led Nernst and Schwers[3] to devise the second type of the vacuum calorimeter. The calorimeter was of copper and the heater a constantan wire. The constantan wire possesses the great advantage that even at low temperatures its temperature coefficient of resistance is negligible and hence the current and the voltage across it can be conveniently adjusted. The temperature was measured with a thermocouple. The calorimeter was surrounded by a copper sheet. For further details the reader is referred to Nernst's *The New Heat Theorem*, pages 37-49.

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[1] For an account of how it is done see *The New Heat Theorem* by Nernst, pp. 46-47 published by Methuen & Co.

[2] *Verb. d. Deuts. Phys. Ges.*, **15**, 578.

[3] *Ber. d. kgl. Pr. Akad. d. Wiss.*, 1914.

In the foregoing experiments the radiation correction had to be determined and applied. A different procedure, however, has been adopted by Simon and Lange.[1] They prevented any loss of heat by devising the "adiabatic vacuum calorimeter". In this apparatus the object is achieved by surrounding the vacuum calorimeter with a bath whose temperature is varied and kept always equal to that of the calorimeter.

The vacuum calorimeter method has been used by a large number of workers. Eucken, Hauck,[2] and Keesom and Onnes used it to find the specific heat of liquefied gases. Clusius and Harteck[3] measured the specific heat of various substances up to 10°K while Sucksmith and Potter[4] found the specific heat of ferromagnetic substances up to about 400°C.

2·22. An ingenious though not very accurate method of finding the specific heat of metals has been used by Corbino[5], Pirani, Worthing[6] and others. The metal is in the form of a uniform wire enclosed in an evacuated glass bulb and heated electrically. The characteristic equation is

$$iE = f(T) + ms\frac{dT}{dt}, \qquad (21)$$

where i and E denote the instantaneous values of the electric current and the voltage across the filament, T its temperature, m its mass, s its specific heat, and dT/dt the rate of rise of temperature. The first term denotes the electrical energy supplied, the second the heat lost by radiation and the third the amount of heat required to raise the temperature of the filament. E and i are measured with a potentiometer and T is calculated from the resistance of the filament. $f(T)$ can be obtained by finding the value of Ei for no rise of temperature. The loss of heat by conduction along the leads was eliminated by performing experiments with wires of different lengths but having the same cross-section and carrying the same current. The radiation generally lags behind the temperature as recorded by a resistance thermometer and hence s as calculated from (21) is different for rising and falling temperatures. The mean of the two values is taken.

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[1] *Zeits. f. phys. Chem.*, **110**, 343, 1924.

[2] *Zeits. f. phys. Chem.*, **134**, 161, 1928. [3] *Ibid.*, **134**, 243, 1928.

[4] *Proc. Roy. Soc.*, **112**, 157, 1926.

[5] *Phys. Zeits.*, **11**, 413, 1910; **14**, 915, 1913 and connected papers.

[6] *Phys. Rev.*, **5**, 340, 1915.

2·23. Heating by Cathode Rays.—An interesting method has been employed by Klinkhardt[1] in which the experimental substance is heated by bombardment with slow cathode rays. His apparatus is indicated in Fig. 13.

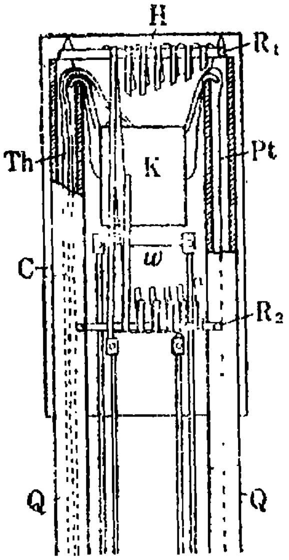

Fig. 13.—Klinkhardt's apparatus.

The experimental metallic substance K is supported in high vacuum by means of two small quartz rods which insure its insulation from the surroundings. Just opposite K is a thoriated tungsten wire w which is heated by a small battery of accumulators. Between w and K an electrostatic field of gradient between 100—200 volts is applied. Thus the electrons from w bombard K which is heated by the kinetic energy of the impact. Any reflection of the electrons is prevented by the electrostatic field between w and K and also between K and the protecting cage C, the latter being kept connected to w. The experimental substance K can be maintained at any desired temperature by passing a suitable current through the heater H which is simply a platinum wire wound over a quartz frame R_1R_2. The loss of heat by radiation to the outer cage is minimised by inserting a platinum sheet between C and K. The temperature of the substance is measured by the thermocouple Th. The whole apparatus was enclosed in an evacuated glass sphere (not shown) the lower end of which was cooled, and upon this rested two stout quartz tubes Q, Q which served to support the whole apparatus and also carried the connecting wires.

Apart from small corrections due to the fact that electrons possess a definite heat of vaporisation the energy supplied was given by the product of the potential gradient and the electron current, the latter being measured by a precision ammeter. Knowing the heat capacity of K, the increase in its temperature and the time of flow of electrons, the specific heat can be calculated. With this apparatus the specific heat of metals could be measured upto 1000°C. correct to about 2 per cent. The apparatus can be adopted to low temperatures.

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[1] *Ann. d. Physik*, **84**, 167, 1927.

Another interesting method has been employed by Davies and Thomas[1] in which the specimen is heated by eddy currents produced in it when placed in an alternating magnetic field. The method has been utilised for determining the specific heat of a number of metals at 20°C and appears to yield satisfactory results.

2·24. Results of Early Experiments.—In 1819 Dulong and Petit from their investigations concluded that the *product of atomic weight and specific heat is constant for many substances*, or in other words, *atoms of all substances have the same capacity for heat.* Regnault from his own researches found that for ordinary substances the mean value of the constant was 6·38 with extremes of 6·76 and 5·7. A more accurate value of the constant can be obtained from the kinetic theory (Chap. III). The atomic heat at constant volume is shown there to be equal to $3R = 5{\cdot}955$. According to Richarz, the value of the ratio C_p/C_v for many substances lies between 1·01 and 1·04, hence the atomic heat at constant pressure, the quantity commonly determined should lie between 6·01 and 6·19. This law is of great use in determining atomic weights.

In illustration of the law we append below table 2 giving the

Table[2] 2.—*Illustration of Dulong and Petit's law.*

Element	Atomic weight (1)	Mean specific heat (2)	Atomic heat (1)×(2)
Sodium ..	23·00	0·703	7·06
Magnesium ..	24·32	0·247	6·00
Aluminium ..	27·1	0·2175	5·83
Iron ..	55·84	0·110	6·14
Nickel ..	58·68	0·1092	6·41
Copper ..	63·57	0·0930	5·92
Zinc ..	65·37	0·0939	6·14
Silver ..	107·9	0·0559	6·03
Cadmium ..	112·4	0·0557	6·26
Tin ..	118·7	0·0556	6·60
Antimony ..	121·8	0·0502	6·10
Platinum ..	195·2	0·0318	6·21
Gold ..	197·2	0·0309	6·10
Lead ..	207·2	0·0310	6·43
Bismuth ..	209·0	0·0299	6·22

Mean value = 6·24

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[1] *Phil. Mag.*, **24**, 713, 1937.

[2] Taken from *Handbuch der Experimental physik*, **8**, p. 193.

mean specific heat of a few elements between 15° and 100°C. The elements are arranged in order of their atomic weights.

In 1831 Neumann enunciated a similar law concerning molecular heats: the *product of the specific heat and the molecular weight of compounds of similar composition are nearly constant.* The value of the constant varies from one series of compounds to another. This law is known as Kopp-Neumann's Law. In illustration of the law the following table[1] is added.

Table 3.—*Molecular Heat of Oxides*

Compound	Specific heat (1)	Molecular weight (2)	Molecular heat (1)×(2)
Cr_2O_3 ..	0·1796	152·0	27·4
Fe_2O_3 ..	0·1700	159·8	27·2
As_2O_3 ..	0·1277	197·8	25·3
Sb_2O_3 ..	0·0901	287·8	25·9
Bi_2O_3 ..	0·0605	464·8	28·1

Mean value = 26·8

Kopp-Neumann's law can be considered as a particular case of the following law: *The molecular heat of a compound may be considered as the sum of the atomic heats of its constituents.* Thus if a compound has the composition $A_aB_bC_cD_d$ its molecular heat C_p is given by the relation

$$C_p = aC_{pA} + bC_{pB} + cC_{pC} + dC_{pD}, \qquad (22)$$

where A, B, C, D stand for the different types of atoms composing the compound and C_{pA}, C_{pB}, etc., their atomic heats given by Dulong and Petit's Law. The law is of much use in evaluating the molecular heats of certain substances.

2·25. Variation of Specific Heat.—The specific heat as determined by the foregoing methods is not found to be a constant quantity. For solids and liquids the effect of pressure on specific heat is rather small. The effect of temperature is however very marked. Increase of temperature invariably increases the specific heat, while the decrease of temperature lowers it. In chapter XVI a table is given which shows the variation of specific heat of silver with temperature. Various empirical formulæ have been proposed from time to time to indicate the effect of pressure and temperature on the specific heat. The effect of pressure can be calculated with the help of thermodynamic formulæ (Chap. VII) while the variations with temperature have been to some extent successfully accounted for only in recent years by the application of the quantum theory of specific heats (Chap. XVI). The earlier observations (*viz.*, Dulong and Petit's law) can be easily accounted for by the kinetic theory (Chap. III) or more accurately by the quantum theory (Chap. XVI).

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[1] Taken from *Handbuch der Experimental physik*, **8**, p. 200.

2·26. Two Specific Heats of a Gas.—The specific heat of a gas, as of solids and liquids, may be defined as the ratio of the heat absorbed to the rise in temperature, per unit mass of the gas. A little consideration will show that this definition is somewhat vague and requires to be more precisely defined. Imagine a quantity of gas to be suddenly compressed. The temperature of the gas will be found to rise though no heat has been added. The ratio, *heat added/increase in temperature*, *i.e.*, specific heat, vanishes. Again let this compressed air expand suddenly ; a cooling would take place. This is just prevented by applying some heat to the gas. In this case the ratio, *heat added/change in temperature*, becomes infinite. Thus we see that the original definition gives an infinite range of values for the specific heat. Hence external conditions are of paramount importance in considering the specific heat of gases. It has become customary to speak of two specific heats of a gas : the *specific heat at constant volume* denoted by c_v and the *specific heat at constant pressure* denoted by c_p. In the former process the gas is maintained at constant volume so that the whole heat applied goes to increase the internal energy[1] of the gas. In the latter case the gas is allowed to expand against a constant pressure and in so doing it does *external work* as well as a very small amount of *internal work* against molecular attractions. These two quantities of work are obtained from the heat energy applied to the gas. Hence the specific heat at constant pressure is necessarily greater than the specific heat at constant volume by an amount which is simply equal to the thermal equivalent of this work.

Let us assume that the gas is perfect, *i.e.*, its molecules exert no influence on one another except during collision. This is approximately true for permanent gases as Joule's experiment (sec. 2·27) shows. Hence in this expansion no internal work against molecular attractions is done by the gas and the excess of heat supplied in the second case is simply the thermal equivalent of the external work.

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[1] According to the molecular point of view internal energy consists of the kinetic and potential energies of the molecules, atoms, electrons etc. For a formal definition of internal energy see Chap. V.

Consider the gas enclosed in a vessel of any shape and suppose the walls of the vessel can expand outwards. Let δA denote an element of area of the walls and δx the distance traversed by it measured along its outward drawn normal. Then the work done by the gas in this infinitesimal expansion is $p\delta A.\ \delta x$ and for the expansion of the entire surface the work is equal to $\Sigma p\delta A.\ \delta x = p\,\Sigma\,\delta A.\ \delta x = p\ \delta V$ where δV is the increase in the volume of the gas and p is the pressure of the gas which remains constant. Suppose a gramme molecule of the gas, occupying a volume V_1 at temperature T°K and pressure p, expands to a volume V_2 at temperature $(T+1)$° K the pressure remaining constant. The work done by the gas in expanding from V_1 to V_2 is

$$p(V_2-V_1) = \mathrm{R}[(T+1)-T] = \mathrm{R} \quad . \quad (23)^1$$

by the gas laws[2]. Let $Mc_p = C_p$, $Mc_v = C_v$, where M is the molecular weight of the gas. C_p and C_v may be called the *gram molecular* or *molar specific heats.* Then the thermal equivalent[3] of the above work is $J\,(C_p-C_v)$. Hence

$$J\,(C_p-C_v) = \mathrm{R}.$$

If C_p and C_v are measured in ergs[4] we get

$$C_p-C_v = \mathrm{R}. \quad . \quad . \quad . \quad . \quad (24)$$

This law was first deduced by R. Mayer.

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[1] This is true for a perfect gas only. For real gases and in fact for any substance it is shown in Chap. VII that

$$C_p-C_v = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial V}{\partial T}\right)_p$$

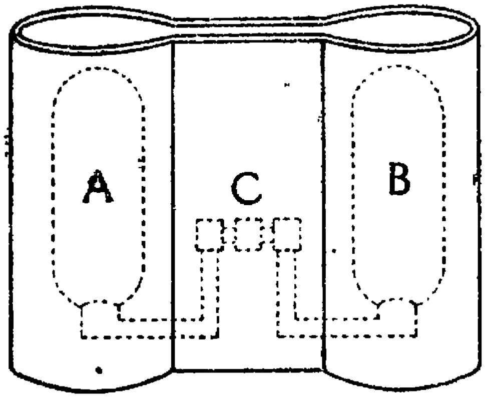
where the differentials must be evaluated from the actual equation of state (Chap. X) for the gas. This is done in Chap. VII.

[2] In applying the gas laws for the relation between V and T we necessarily assume that the gas is always in a state of equilibrium and never passes through non-equilibrium states. Such a process is called a *quasi-static* process which is characterised by the condition that the system is at all times infinitesimally near a state of mechanical and thermal equilibrium with the surroundings as well as with its own component parts.

[3] This assumes the First Law of Thermodynamics which will be discussed in Chap. III and Chap. V.

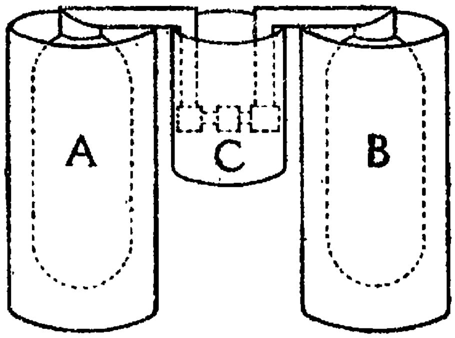
[4] For a more formal proof see Chap. V.

2·27. Experiments of Gay-Lussac and Joule.—Gay-Lussac first carried out experiments to determine whether a gas does any internal work in expanding. Somewhat later Joule employed a similar apparatus but he immersed the vessels in calorimeters. His apparatus is indicated in Figs. 14 and 15. The two vessels A and B communicated with each other through a tube furnished with a stop-cock C. A was filled with dry air at 22 atmospheres while B was exhausted. First the whole apparatus was placed in a single calorimeter (Fig. 14) and the stop-cock C opened allowing the enclosed gas to expand. This process is called *free expansion* as no external pressure is applied to the gas. Joule could not detect any change in the temperature of the water, showing thereby that no internal work against molecular attractions was done by the gas in expanding. To investigate the point further, the parts A, B, C were placed in separate vessels (Fig. 15) containing water whose temperatures could be read by sensitive thermometers. On opening the stop-cock C the air expanded into B and the temperature of the vessel surrounding A fell while the temperatures of B and C rose. It was found that the heat lost by A was equal to the sum of the heats gained by B and C, thus the total change in the energy of the gas during expansion is zero, *i.e.*, $(\partial U/\partial V)_T = 0$ where U is the internal energy and V the volume. This is known as Mayer's hypothesis or Joule's law. This shows clearly that no internal work is done by a gas in expanding. Joule's law holds only for the perfect gas to which the permanent gases of nature like helium, hydrogen, etc. approximate. For further discussion



Joule's experiment with one calorimeter

Fig. 14.



Joule's experiment with two calorimeters

Fig. 15.

see Chap. XII. As a matter of fact a slight fall in temperature should be observable in Joule's experiment with one calorimeter but on account of the large heat capacity of the calorimeter it escaped detection.

2·28. Adiabatic Transformations.—When a system undergoes a change under the condition that no heat enters or leaves it, the transformation is said to be *adiabatic*. Such a process can be approximately realised in practice by thermally insulating the system with some non-conducting material, or by performing the process rapidly since in general heat conduction takes place very slowly. In an isothermal change the temperature is kept constant by adding heat to or taking it away from the substance. In general a process must be performed very slowly in order that it may be isothermal. Consider an amount of heat δQ applied to a perfect gas. As shown in sec. 2·26 this is spent in raising the temperature of the gas and in doing external work. If we consider a gramme molecule of the gas, the former is equal to $C_v\,dT$ and the latter to pdv/J both in calories. Hence

$$\delta Q = C_v dT + \frac{pdV}{J},$$

or, if δQ and C_v are measured in ergs,

$$\delta Q = C_v dT + pdV. \quad . \quad . \quad . \quad . \quad (25)$$

This equation combined[1] with $pV = RT$ will give the solution of all problems on perfect gases. In an adiabatic transformation $\delta Q = 0$. Therefore

$$C_v dT + pdV = 0. \quad . \quad . \quad . \quad . \quad (26)$$

In order to find a relation between p and V we must eliminate T from (26) by means of the gas equation $pV = RT$. Differentiating the latter, we have

$$p\,dV + Vdp = \mathrm{R}\,dT. \quad . \quad . \quad . \quad . \quad (27)$$

Substituting for dT from (27) in (26), and replacing R by $C_p - C_v$, we get

$$C_v\,Vdp + C_p\,p\,dV = 0.$$

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[1] When we use the equation of state $pV = RT$ we necessarily imply that the process is quasi-static or mechanically reversible.

Denoting C_p/C_v by γ we obtain

$$\frac{dp}{p} + \gamma \frac{dV}{V} = 0,$$

which on integration yields

$$\log p + \gamma \log V = \textit{constant},^1$$

or

$$p\, V^{\gamma} = \textit{constant}. \quad . \quad . \quad . \quad . \quad . \quad (28)$$

This is the relation between p and V for quasistatic adiabatic changes in a perfect gas[2]. In such changes the gas must pass through equilibrium states. It may be pointed out that a free expansion is adiabatic but not quasistatic and it is fallacious to apply equation (28) to such a process, though this is frequently done.

To find the quasistatic adiabatic relation between T and V or between T and p we must respectively eliminate[3] p or V between equation (28) and the gas equation $pV=RT$. The results are

$$TV^{\gamma-1} = \textit{constant}; \quad . \quad . \quad . \quad . \quad . \quad (29)$$

$$Tp^{(1-\gamma)/\gamma} = \textit{constant}. \quad . \quad . \quad . \quad . \quad . \quad (30)$$

2·29. Experimental Methods.[4]—We shall now consider the experimental methods of finding the specific heats of gases. Since for perfect gases $C_p - C_v = R$, a knowledge of one of the specific heats gives the other. Again if we determine γ, *i.e.*, C_p/C_v, the

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[1] We have assumed that γ remains constant in the integration. Strictly speaking this is not the case. C_v and hence C_p and γ also, vary with volume, pressure and temperature of the gas. Hence equations (28), (29) and (30) do not hold rigorously for all values of p, V, and T. The differential equations however are quite exact and the integrated results will also be exact for small variations of the variables in which γ could be treated as constant. We have of course to substitute the proper value of γ under the conditions of pressure, volume and temperature.

[2] For real gases the relations corresponding to (28), (29) and (30) are much more complicated and cannot be deduced without making use of both the laws of thermodynamics. These relations can be deduced by starting from the results obtained in examples (1), (2) and (3) at the end of Chap. VII. This is illustrated in example (4) following them. For experimental measurements of γ based on the adiabatic expansion method (§2·37—2·40), these equations deduced there for actual gases must be used.

[3] Equation (29) can be deduced more briefly by eliminating p between (26) and the equation $pV = RT$, and equation (30) by eliminating dV between (26) and (27).

[4] The reader will find a very good account of these methods in Partington and Shilling, *Specific Heat of Gases.*

above relation will give both C_p and C_v. Hence the experimental methods may be divided into three classes: (*a*) The measurement of C_p, (*b*) The measurement of C_v, (*c*) The determination of γ.

(*a*) MEASUREMENT OF C_p.

The specific heat at constant pressure has been found either by the Method of Mixtures or by the Constant-Flow Method. The principle of these methods has been already explained.

2·30. Method of Mixtures—Regnault's Apparatus.—This method was first applied to gases by Lavoisier and Laplace and was later used by Regnault who obtained results of high accuracy. His apparatus is indicated in Fig. 16. Pure dry gas was compressed in the reservoir A which was immersed in a thermostat. The reservoir was provided with a manometer (not shown). Gas could be allowed to flow through the stopcock V at a uniform rate. This was effected by continuously adjusting the stop-cock V (shown separately in Fig. 16*b*) so that the pressure indicated by the manometer R was constant. The gas then flowed through a spiral S immersed in a hot oil-bath and then into the calorimeter C finally escaping into the air. The gas acquired the temperature

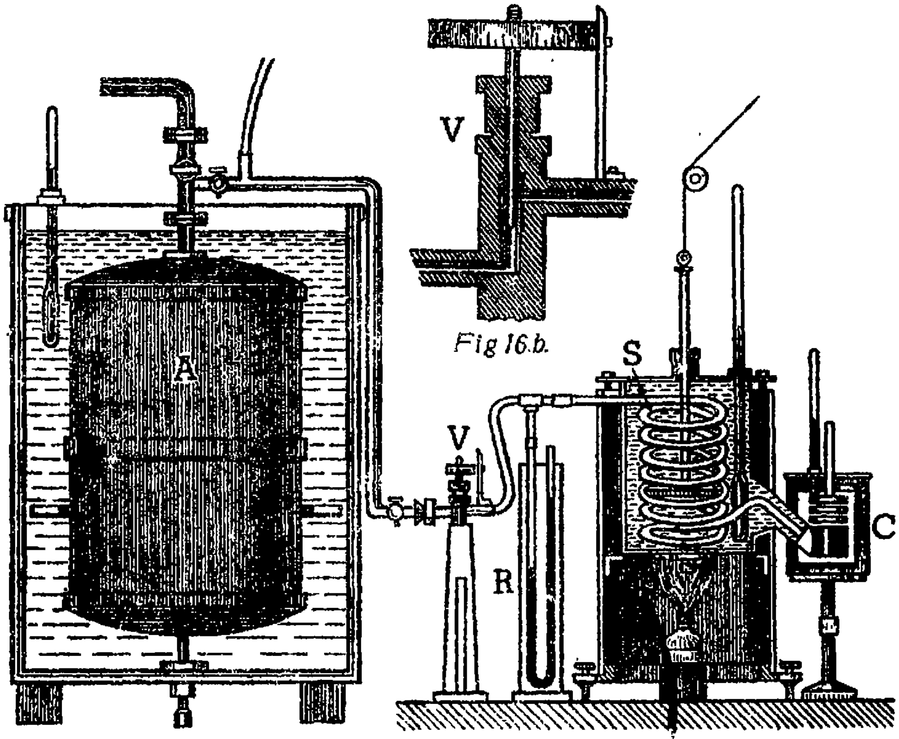

Fig. 16.—Regnault's Apparatus for C_p.

T of the bath and raised the temperature of the calorimeter, say from θ_1 to θ_2.

If m be the mass of the gas that flows into the calorimeter, c_p its specific heat is given by

$$mc_p\left(T-\frac{\theta_1+\theta_2}{2}\right)=W(\theta_2-\theta_1), \quad . \quad . \quad . \quad (31)$$

where W is the thermal capacity of the calorimeter and its contents.[1]

2·31. Other Experiments.—The experiments of Wiedemann (1876) were essentially similar to those of Regnault. Lussana (1898) devised a high-pressure apparatus in which the same amount of gas enclosed at a high pressure can be repeatedly heated and passed through the calorimeter. The principle employed is the same as in Regnault's experiment. McCollum[2] has employed this method for measuring the specific heat of dissociating N_2O_4 between room temperature and 100°C.

As regards determination of specific heat at high temperatures the experiment of Holborn and Henning[3] may be mentioned. Employing suitable electric heaters and a well-designed calorimeter they were able to find the specific heats of nitrogen, carbon-dioxide and steam up to 1400°C. The calorimeter corrections are difficult and uncertain. The same method has been used by Nernst[4] in finding the specific heat of ammonia up to 600°C.

2·32. Constant-flow Method.—For finding the variation of specific heat with temperature the constant-flow method is most suitable and was first used by Swan.[5] Scheel and Heuse[6] used the method for finding the specific heat down to very low temperatures.

Their calorimeter is indicated in Fig. 17.T he gas under test, previously brought to a steady temperature by passing through a suitable bath, enters the calorimeter from below at E and flows in a steady stream through a spiral F, then through two jackets C and B as indicated by the arrows and finally enters the inner tube at A. This gas is now heated by the heating coil H made of constantan. The temperatures of the incoming and outgoing gases are observed by the resistance thermometers T_1, T_2. Above the heater are a wire gauze G_1 and a packing of wire gauze G_2 (shown separately) in order to make the temperature of the gas uniform before reaching the thermometer T_2. The gas leaves the apparatus as indicated. Nearly the whole apparatus is enclosed in an evacuated jacket D, the latter itself being immersed in a constant temperature bath. When the gas flows through the jackets C and B it absorbs much of the heat radiated out and thus the radiation loss is considerably diminished.

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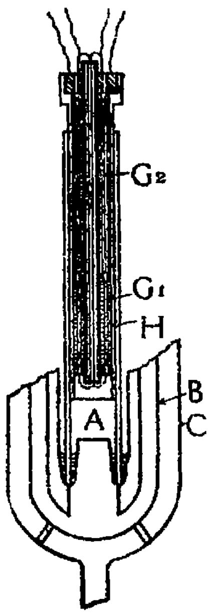
[1] A detailed theory of this method which is applicable to all flow methods has been given by Searle, *Proc. Camb. Phil. Soc.*, **13**, 321, 106.

[2] *Jour. Amer. Chem. Soc.*, **49**, 28, 1927.

[3] *Ann. d. Physik*, **23**, 809, 1907. [4] *Zeits. f. Electrochemie*, **16**, 96, 1910.

[5] *Proc. Roy. Soc.*, A, **82**, 147, 1909 ; or *Phil. Trans.*, A, **210**, 199, 1910.

[6] *Ann. d. Physik*, **37**, 70, 1912; **40**, 473, 1913; **59**, 86, 1919.



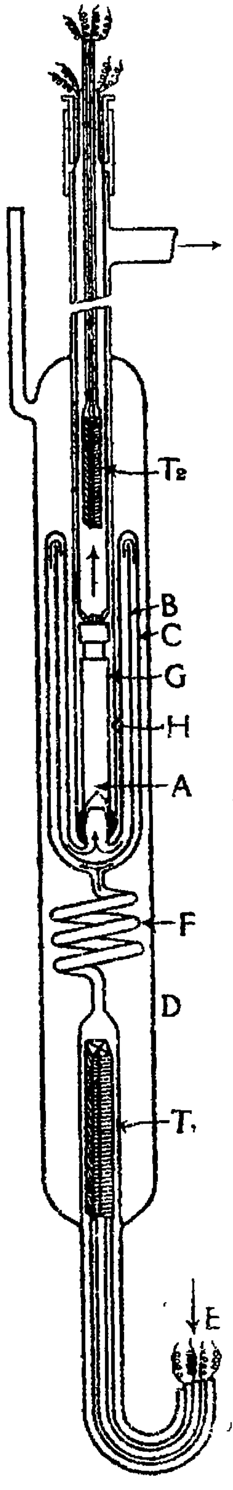


Fig. 17.—Constant-flow Calorimeter for gases.

The equation for continuous flow already given is

$$Eit = JM's\ \delta\theta + H.$$

If m grams of the gas flow in 1 second and M denote its molecular weight, C_p its molar specific heat and h the heat loss per second, the above becomes

$$\frac{JmC_p}{M}\delta\theta = Ei - h. \qquad . \quad . \quad (32)$$

The greater part of the heat lost is brought back by the incoming stream of gas. To calculate the true heat loss we proceed as follows: The heat h' lost by the gas and heater to the surrounding vessel is proportional to $\delta\theta$ and assuming Newton's law, it may be put equal to $k_1\delta\theta = k_1'Ei/m$. This will produce a rise in temperature of the surrounding gas equal to $\delta\theta'$ which is proportional to h'/m. Thus $\delta\theta' = k_2Ei/m^2$ and the heat lost by radiation from this to the bath surrounding D will be $k_3\delta\theta' = kEi/m^2$ for $\delta\theta'$ represents the excess of temperature of C and the outer gas over the bath as the gas was initially brought to the temperature of the bath. Hence $h = kEi/m^2$ where k is some constant. Equation (32) then yields

$$C_p = \frac{M\,Ei}{Jm\,\delta\theta}\left(1 - \frac{k}{m^2}\right). \qquad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

k can be eliminated by performing experiments with different values of m.

For work at low temperatures the gas was initially passed through a low temperature bath in which the calorimeter was also immersed. In studying helium and other rare gases Scheel and Heuse modified the apparatus so as to employ a closed circuit. They carried out measurements on various gases in the range 0 to 180°C., and found reliable results. The theoretical explanation for the variation of specific heat with temperature is given in Chap. XVI.

For measurement of specific heat at high pressures the constant-flow method has been employed by Holborn and Jakob[1], Krase and Mackey[2] and others and gives the most reliable results. It may, however, be pointed out that the constant-flow method always gives values about 1 per cent. higher than those obtained by adiabatic expansion or acoustic methods (§2·37—2·44).

2·33. A modified Constant-flow Method.—In the foregoing constant-flow method there is much difficulty and uncertainty in measuring the temperatures of the inflowing and outflowing gas. This has been avoided in a new type of constant-flow apparatus devised by Blackett, Henry and Rideal[3] which is, however, based on different principles. In this a knowledge of the temperature of the gas is not at all necessary. The principle of the experiment will be explained by considering a simplified[4] case.

Consider a long narrow tube with its two ends kept at temperatures differing by θ_1 and suppose radiation from the sides of the tube is prevented. Then, as will be shown in Chap. XIV, there will be a uniform temperature gradient along the tube equal to θ_1/l where l is the length of the tube. If now a gas is allowed to flow slowly through the tube from the cold end to the hot end, it will acquire heat by conduction from the walls and will be continuously rising in temperature as it goes forward. Let ϕ denote the excess of the temperature of the gas at any section over the temperature of the cross-section of the tube at the same place. Then $\phi=0$ at the ends and except for a small distance near the ends, it has a constant negative value $\bar{\phi}$ throughout the tube, since $\bar{\phi}$ can depend only on the gradient $d\theta/dz$, the radius of the tube (both of which are constant) and the velocity of flow v_0, the viscosity, conductivity, density and specific heat of the gas, and all these can be treated as constant as long as θ_1 is small.

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[1] *Berl. Ber.*, **1**, 213, 1914.

[2] *Am. Chem. Soc. J.*, **52**, pp. 108 and 5111, 1930.

[3] *Proc. Roy. Soc. Lond.*, **126**, 319, 1930; see also Henry, *Ibid.*, **133**, 492, 1931.

[4] For a detailed consideration of the theory of the method and its verification the original paper should be consulted.

The temperature rise of the gas per second is $v_0\, d\theta/dz$. If r be the radius of the tube and s the specific heat of the gas per unit volume at constant pressure, the heat necessary to maintain the rise in temperature of the gas contained in unit length of the tube is

$$Q = \pi r^2\, s v_0 \frac{d\theta}{dz} = s V_0 \frac{d\theta}{dz}, \qquad (34)$$

where $V_0 = \pi r^2 v_0$ the volume of gas passing per unit time. This heat Q is supplied by the wall per unit length per unit time, and on account of this the temperature gradient will change. The heat gained[1] by the element through conduction is $KA d^2\theta/dz^2$ where K is the thermal conductivity of the tube and A the area of its cross-section. Hence in the steady state

$$KA \frac{d^2\theta}{dz^2} - sV_0 \frac{d\theta}{dz} = 0. \qquad (35)$$

Assuming this equation to hold up to the ends of the tube (which is not so since ϕ changes there), the solution of (35) with the boundary conditions $\theta = 0$, when $z = 0$, $\theta = \theta_1$ when $z = l$, becomes

$$\theta = \theta_1 \frac{1 - e^{2az}}{1 - e^{2al}}, \qquad (36)$$

where $a = sV_0/2KA$. Assuming a to be small, for $z = l/2$ this gives

$$\theta = \theta_1 (1 + e^{al})^{-1}$$

and its excess Θ over the temperature $(\theta_1/2)$ prevailing there without flow is given by

$$\Theta = -\theta_1 a l/4 = -sV_0\theta_1 l/8KA. \qquad (37)$$

Thus the ratio of the quantity Θ/V_0 for two gases will be in the ratio of their specific heats.

The relation (34) will hold even if the tube is surrounded by a bath having the temperature of the cold end and also for large values of θ_1.

For experimental purposes it is more convenient to have a long tube whose ends are kept at the same temperature, and the central portion is raised to the maximum temperature by an electric current passing through the entire rod. The previous temperature difference Θ is now analogous to the present temperature difference between the midpoints of the two bars (to which the present bar is equivalent), and can be shown to be given by

$$\Theta = C_1 a + C_3 a^3 + \ldots, \qquad (38)$$

---

[1] See Chap. XIV.

where C_3 depends upon conductivity, viscosity, etc., of the gas, and the high power terms become appreciable only for large velocities of flow of the gas.

A section of their apparatus is shown in Fig. 18. The experimental gas flows through the narrow iron tube AA, 2 mm. in diameter, which is further surrounded by the massive iron tube BB the latter having conical holes at the ends to fit the conical steel plugs C, C. These are held in position by the screwed collars D, D and are electrically insulated from B by mica. The conical plugs C, C carry the cylindrical plugs E, E which fit tightly on AA. The whole apparatus is enclosed in a furnace. The thin constantan wires, which, with the tube AA form the thermo-couples, are embedded in AA, one at the centre, two at equal distances on either side of the middle point, and one at the end; these are all carried in porcelain tubes through holes in E. The tube AA is heated by an alternating electric current which is kept constant by an automatic regulator. By moving the screws S, S it is so arranged that the symmetrical thermo-couples, connected differentially record zero deflection on a potentiometer arrangement. The gas is next allowed to flow through AA at a slow speed, which is maintained constant by a complex device, and the value of Θ obtained from the readings of the symmetrical thermo-couples. The maximum temperature θ_m developed in the centre was also observed, and the mean value of $\Theta / V_0\theta_m$ for different gases was found. The ratio of this quantity for different gases gives the ratio of their specific heats and knowing the specific heat of one (say argon) the specific heat of O_2, N_2 and air was found up to 350°C. The accuracy claimed by the experimenters is about 1 per cent.

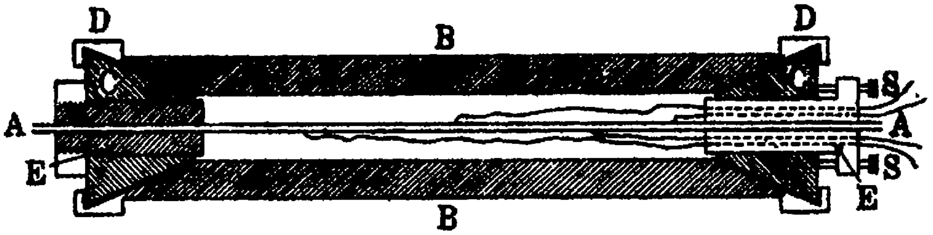

Fig. 18.—Henry's modified constant-flow apparatus.

(*b*) METHODS BASED ON THE MEASUREMENT OF C_v

2·34. Steam Calorimeter.—The direct determination of C_v is best made by means of Joly's steam calorimeter (Sec. 2·13). The method of carrying out the experiment and the necessary details will be found in that section.

2·25. Explosion Method.—Following the work of Bunsen, Vieille and others, Pier[1] improved the explosion method and devised the modern explosion bomb shown in Fig. 19. Immersed

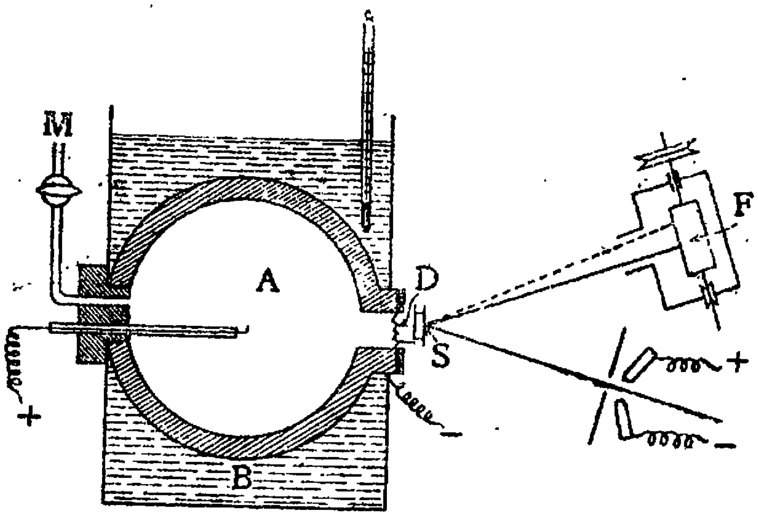

Fig. 19.—Pier's Explosion Bomb.

in the water-bath B is a steel-bomb A which has side-tube M through which the bomb can be evacuated and various gases introduced at the desired partial pressures. D is a corrugated steel membrane closing an opening in the bomb and carrying mirror S. Light reflected from the mirror falls on the photographic film F which is wound on a revolving drum. By applying various known static pressures and noting the deflection of the light spot, the pressure attained in any experiment can be found simply from the record on the film. Any explosion mixture, say a mixture of hydrogen and oxygen, together with the inert gas whose specific heat is required is introduced into the bomb. By 'inert' is meant any gas which will not take part in the reaction either from want of chemical affinity or due to its presence in excess. The partial pressures of the various gases are known. The explosion is started by means

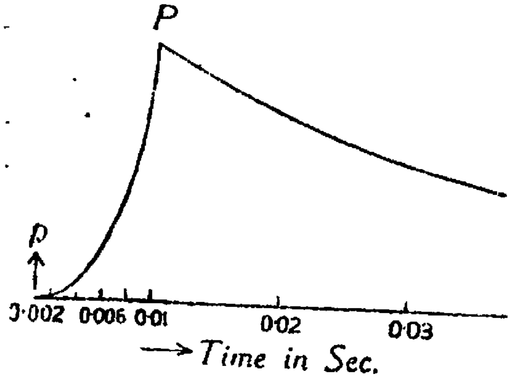

Fig. 20.—Continuous record of pressure during explosion.

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[1] *Zeits. f. Phys. Chem.*, **66**, 795, 1909; *Zeits. f. Elektrochemie*, **15**, 536, 1909; **16**, 897, 1910.

of electric sparks and the record on the photographic film is taken. Fig. 20 shows a typical record. From this the maximum pressure p_1 reached during an explosion can be easily read (corresponding to the point P in the figure). The maximum pressure is reached in about 0·01 sec.

The calculation may be easily made. If the vessel were allowed to cool to the initial temperature T_2 (absolute), suppose it would record the pressure p_2. The maximum temperature T_1 reached during the explosion is calculated from the value of p_1, for, from the gas laws, since the volume remains constant,

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}. \qquad \therefore T_1 = \frac{p_1}{p_2} T_2.$$

Or, if p_i denote the initial pressure and r the ratio final/initial number of molecules (owing to the explosion the total number of molecules changes), we have

$$p_2 = r\, p_i \;\; [\because \text{volume and temperature are the same}]$$

$$\therefore T_1 = \frac{p_1}{rp_i} . T_2 = \frac{p^*}{r} T_2, \qquad \ldots \quad (39)$$

where p^* is the ratio of explosion pressure to initial pressure. The relation connecting the specific heats and the heat of reaction is

$$\mathbf{n}Q_2 = (T_1 \quad T_2)\,(\mathbf{n}C_{vr} + \mathbf{n}'C_{vi}), \qquad \ldots \quad (40)$$

where **n** is the number of gramme-molecules of the reaction products, **n**′ the number of gramme-molecules of the inert gas; C_{vr}, C_{vi} respectively their mean molar specific heats over the range $(T_1 - T_2)$; Q_2 the heat of reaction for the explosion mixture at T_2°. Q_2 is generally known from thermochemical data. We can determine C_{vr} by exploding either with different amounts of a gas whose variation of specific heat with temperature is known, or with different quantities of argon, a substance whose specific heat is constant. Then the same reacting gases may be exploded with any inert gas, and knowing C_{vr} we can find C_{vi} for the inert gas.

The method is very suitable for measurements of specific heat up to high temperatures and has been used to about 3000°C., but suffers from the disadvantage that directly it gives only the average values over a wide range and not the specific heat at any temperature. With numerous data it is possible to calculate the latter, but even the average values are subject to considerable uncertainty, because corrections[1] must be applied for loss of heat, effects of dissociation, incomplete combustion, etc. For argon, Pier found that the specific heat does not vary with temperature.

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[1] See *Zeits. f. Electrochemie*, **17**, 731, 1911; **18**, 101, 1912.

The method has been employed, among others, by Bjerrum (1913), Siegel (1914), Wohl[1], Womersley[2] and Fenning and Whiffen[3]. The last mentioned workers have found the molecular heats of CO, N_2, CO_2 and water vapour. Their results agree with deductions from spectroscopic data.

2·36. Nernst's vacuum-calorimeter method is employed to find C_v at low temperatures. Eucken has in this way found the specific heat of hydrogen between 35° and 273°K and obtained interesting results which will be discussed in Chap. XVI. In his experiments hydrogen was contained in a thin-walled steel flask which was heated electrically by winding round it a constantan wire carrying electric current. The rise in temperature was measured by a resistance thermometer of lead or platinum. It may be remarked that the heat capacity of the containing vessel, which would have been much greater at ordinary temperatures, is only a small fraction at these low temperatures. The same method was employed by Giacomini[4].

(*c*) METHODS BASED ON DETERMINATION OF γ

As already pointed out this is an indirect method of finding the specific heats of gases. Though indirect it is capable of the highest accuracy so that the modern accepted values[5] of specific heats are based on the values of γ thus obtained.

The methods of measuring γ, the ratio of the two specific heats, may be classified under two heads : (1) those depending on the ***adiabatic expansion or compression*** of a gas, (2) those depending on the ***velocity of sound*** in the gas. We shall first consider the former.

(1) ADIABATIC EXPANSION METHOD

2·37. Experiments of Clement and Desormes.—Clement and Desormes (1819) were the first to find γ by the adiabatic expansion method. Their original apparatus has been considerably improved and is indicated in Fig. 21. A large flask A of about 28 litres capacity is closed by a stop-cock M about 1·4 cm. in diameter. The flask is connected to the water manometer P_iP_A by means of a side-tube and is plugged with cotton-wool to avoid loss of heat. First the flask is partially evacuated and the pressure p_i, recorded by the manometer, is observed. The stop-cock M is then opened and quickly closed. Air rushes into the flask till the pressures inside and outside become equal. The process is adiabatic since the loss of heat in the short interval for which the stop-cock M is open, may be neglected. The temperature of the air in the flask rises on account of the inrush of the external air and the pressure becomes atmospheric. The flask is next allowed to cool to the temperature of the surroundings when the water in the manometer rises and finally indicates the pressure p_f.

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[1] *Zeits. f. Phys. Chem.*, **118**, 400, 1925.

[2] *Proc. Roy. Soc. Lond.*, **100**, 483, 1923.

[3] *Phil. Trans.*, A, **238**, 149, 1939.

[4] *Phil. Mag.*, **50**, 146, 1925.

[5] It may be remarked in this connection that an error of 1 per cent. in the value of γ will produce an error of 3 per cent in the value of C_p or C_v which is a serious handicap to this method. Further, see the criticism by Henry, *Proc. Roy. Soc.*, **133**.

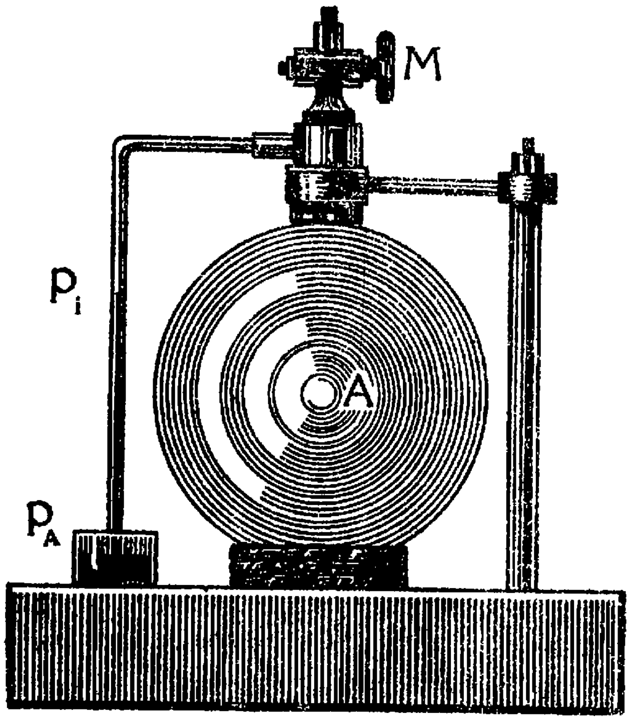

Fig. 21.—Clement and Desormes' Apparatus.

Let the atmospheric pressure be p_A, and the specific volumes of the air at the pressures p_i, p_A, p_f and the corresponding temperatures be v_i, v_A, v_f respectively. The first process is adiabatic and if, in addition, we assume it to be approximately quasistatic, we have in the case of a perfect gas,

$$p_i v_i^{\gamma} = p_A v_A^{\gamma} \quad . \quad . \quad . \quad . \quad . \quad (41)$$

Since the final temperature is the same as the initial, we have, considering 1 gram of the gas

$$p_i v_i = p_f v_f \quad . \quad . \quad . \quad . \quad . \quad (42)$$

Again

$$v_A = v_f, \quad . \quad . \quad . \quad . \quad . \quad (43)$$

because the volume of the manometer tube is negligible compared with that of the flask and hence there will be no appreciable change in the specific volume of the gas due to the rise of the liquid in the manometer.

Combining (41), (42), and (43), we have,

$$\frac{p_i}{p_A} = \left(\frac{p_i}{p_f}\right)^\gamma.$$

Or
$$\gamma = \frac{\log p_i - \log p_A}{\log p_i - \log p_f} \quad . \quad . \quad . \quad . \quad (44)$$

From measurements of Clément and Désormes, Laplace deduced the value of γ to be 1·354.

In this experiment there is a source of serious error. We have assumed that the pressure inside has become atmospheric when the stop-cock M is closed. Actually however oscillations set in; on account of the kinetic energy more air enters in the first rush than would make the pressure just atmospheric, and hence the pressure inside becomes greater than p_A. Next some air rushes out till the pressure inside is less than p_A and so on. After several such overshootings the pressure p_A is attained. This takes considerable time and as a matter of fact, this to-and-fro motion has not subsided when the stop-cock is closed. It must be closed at the instant when during an oscillation the pressure just becomes atmospheric. This is very difficult to secure and hence later investigators tried to avoid it by measuring the change in temperature resulting from adiabatic expansion. The stop-cock has not to be closed in this case. We shall consider shortly the experiments of Lummer and Pringsheim and of Partington and Shilling based on this principle.

We have assumed above that the incoming air has the same temperature as the air in the flask initially. To avoid correction in case it is not so, it is better to start with compressed gas in the flask. Further, care must be taken to use perfectly dry air, for γ is appreciably different for moist air. Consequently the water manometer is replaced by a sulphuric acid gauge. Röntgen (1870) modified the apparatus and determined the cooling during expansion on account of radiation by making use of Newton's law of cooling and corrected his results for it.

2·38. Experiments of Joule, Lummer and Pringsheim, and Partington.—Joule was the first to study the change in temperature by adiabatic expansion or compression. Various investigators later employed this method to determine γ. Air was compressed in a vessel and its temperature and pressure observed. It was then allowed to expand suddenly to atmospheric pressure and the change in temperature noted. The calculations can be easily made. If p_1, T_1 denote the pressure and temperature before expansion, p_2, T_2 the same quantities after expansion, we have, from (30)

$$T_1 p_1^{(1-\gamma)/\gamma} = T_2 p_2^{(1-\gamma)/\gamma} \quad . \quad . \quad . \quad (45)$$

or

$$(1-\gamma)\log\frac{p_1}{p_2} = \gamma\log\frac{T_2}{T_1}.$$

$$\therefore \gamma = \frac{\log p_1 - \log p_2}{(\log p_1 - \log p_2) - (\log T_1 - \log T_2)} \quad . \quad . \quad (46)^1$$

Thus γ can be calculated.

Lummer and Pringsheim[2] made considerable improvements in the apparatus for determining γ by this method. They employed a 90-litre copper sphere and measured the change in temperature by the change in resistance of a thin bolometer[3] wire hanging at the centre of this sphere. A Thomson galvanometer having a period of 4 sec. was used as a null instrument. Certain errors are however inherent in the apparatus :

(1) The bolometer acquires heat from the walls of the vessel by conduction and convection through the gas.

(2) Heat is conducted away along the leads.

(3) The bolometer receives heat radiated by the walls.

(4) The temperature measurement is uncertain on account of the lag of the bolometer and the period of the galvanometer.

In order to eliminate these errors Partington[4] has further improved the apparatus. To reduce (1) a large expansion vessel (130 litres capacity) is used and to reduce (2) thin leads are employed for the bolometer. To eliminate (4) a bolometer of very thin platinum wire (·001 to ·002 mm. in diameter) with compensating leads is employed; thus there is no lag. Further an Einthoven string galvanometer capable of recording tempera-

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[1] As already pointed out, in accurate work we must use, instead of (41) and (45), the equations deduced in example (4) at the end of Chap. VII from the actual equation of state for the gas. The results would then become much more complicated.

[2] *B. A. Reports*, p. 565 (1894).

[3] It is simply a resistance thermometer made of very fine wire.

[4] *Proc. Roy. Soc. Lond.*, A, **100**, 27, 1921.

ure in 0.01 sec. is used so that a detailed record of changes in temperature of the gas during and after expansion is obtained. His apparatus is indicated in Fig. 22. The vessel A is provided with the expansion valve C which can be manipulated by means of the spring P and whose size can also be varied. A is connected to the sulphuric acid manometer M, the mercury manometer *m*, and the drying tubes F. Thus carefully purified air enters A. Further the vessel A is kept immersed in a water-bath which is kept stirred by S. B is the bolometer wire (shown separately in the figure) and is connected in one arm of a Wheatstone bridge. G is the string galvanometer.

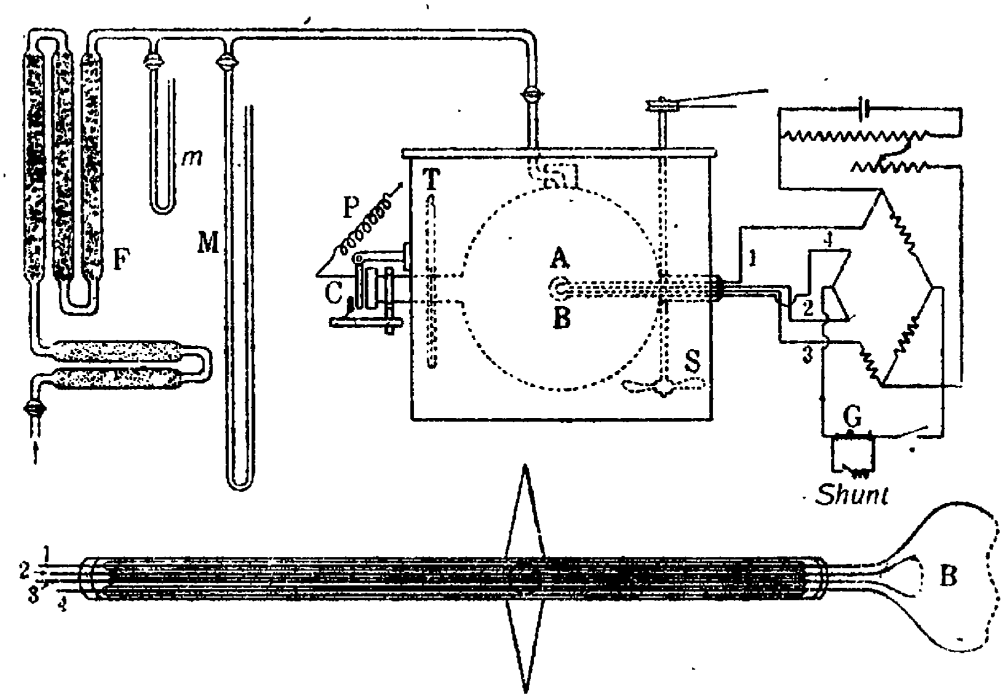

Fig. 22.—Partington's apparatus.

The initial temperature was read on a carefully standardised mercury thermometer T immersed in the bath and was given correct to ·01°. Then the resistance in one arm of the Wheatstone bridge was arbitrarily lowered to give some deflection in the galvanometer. The initial pressure of the gas was so arranged by trials that immediately after expansion this deflection was reduced to zero. After the expansion experiment some ice was continuously added to the bath to keep its temperature constant and equal to that immediately after expansion. This was ascertained by keeping the galvanometer deflection steadily at zero, and the temperature of the bath was again read on the same mercury thermometer.

If the aperture is too large, oscillations of the gas take place and the galvanometer deflection is not quite steady, the initial deflection being somewhat greater than the true value. If the aperture is too narrow prolonged expansion results and the process is not adiabatic. In practice the aperture was gradually diminished and when overshooting was eliminated the deflection was instantaneous, and perfectly steady. The initial pressure of the enclosed gas was read on the manometer M and the atmospheric pressure was read on a Fortin's barometer. γ was calculated in the manner explained above and its value was found to be 1·4034 at 17°C. This method cannot be used at high temperatures since it is impossible to determine accurately the cooling correction.

A further modification of this method has been used by Kistiakowsky and Rice[1] who employed a wollaston wire as a resistance thermometer and a better device for measuring the pressure accurately and rapidly.

2·39. Rüchardt's Experiment.—A simple method for determining γ, which is suitable for class-room demonstration has been described by Rinkel[2] and Rüchardt[3]. Rüchardt's apparatus consists of a large glass bottle V (Fig. 23) fitted air-tight with a glass-tube at the top and a stop-cock H at the bottom. The glass tube has a very uniform bore in which a steel ball of mass m fits very accurately. If the ball is dropped into the tube, it begins to oscillate up and down and comes to rest after a few oscillations. If the period of oscillation be determined with a stop-watch, γ can be easily calculated.

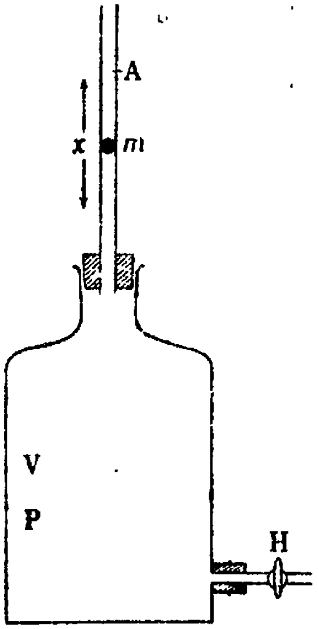

Fig. 23.—Rüchardt's apparatus.

Let A be the cross-section of the glass tube, v the volume of the bottle, p_0 the barometric pressure, and p the pressure in the flask. Then in the equilibrium position

$$p = p_0 + \frac{mg}{A}. \qquad (47)$$

If the ball now moves a distance x downwards, it compresses the air adiabatically increasing the pressure to $p+dp$, hence its equation of motion is

$$m\frac{d^2x}{dt^2} = -Adp. \qquad (48)$$

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[1] *Jour. Chem. Phys.*, **7**, 281, 1939.

[2] *Phys. Zeits.*, **30**, 805, 1929.

[3] *Phys., Zeits.*, **30**, 57, 1929.

Now since pv^{γ} = constant, we have

$$dp = -\gamma p \frac{dv}{v} = \gamma p \frac{Ax}{v} \quad . \quad . \quad . \quad . \quad (49)$$

$$\therefore\ m \frac{d^2x}{dt^2} = -\frac{\gamma p A^2}{v} x, \quad . \quad . \quad . \quad (50)$$

from which the period of oscillation comes out to be

$$T = 2\pi \sqrt{\frac{mv}{\gamma p A^2}}\,; \quad \text{or } \gamma = \frac{4\pi^2 mv}{pA^2T^2}. \quad . \quad . \quad (51)$$

Thus knowing T, p, and the constants of the apparatus, γ can be evaluated.

Due to insufficient number of oscillations considerable error creeps in and hence Rüchardt's results were not very accurate. Brodersen[1] has developed a photographic arrangement for measuring the periodic time correct to about 0·1 per cent. and claims an accuracy of 0·3 per cent. in the value of γ. Light from a mercury vapour lamp at 500 cycles was placed behind the tube in which the ball was oscillating. The light after traversing the tube fell on a rotating mirror from which it was reflected on to a photographic plate. Thus the motion was automatically recorded on the photographic plate and the photograph enlarged, and from this the periodic time could be accurately read.

Another modification has been employed by Clark and Katz[2] who caused oscillations of a steel piston separating two gas chambers. The oscillations were produced by an alternating magnetic field produced by an alternating current in a coil, the frequency of alternating current being varied to get resonance. The results obtained by this method are quite accurate and reproducible.

(2) VELOCITY OF SOUND METHOD

2·40. This method also depends upon the adiabatic expansion and compression of a gas but differs from the foregoing method in that no direct measurement of changes in temperature or pressure need be observed. The method has given us very accurate data regarding specific heats for both high and low temperatures and so we shall consider it in some detail.

The velocity of sound $\mathcal{V}$ in any fluid is given by the equation[3] $\mathcal{V} = \sqrt{E_s/\rho}$ where E_s is the adiabatic elasticity of the fluid and ρ its density. For adiabatic changes in perfect gases pv^{γ} = constant, hence

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[1] *Zeits. f. Physik.*, **62**, 80, 1930.

[2] *Can. Jour. Res.*, A, **18**, 23, 1940; **21**, 1, 1943.

[3] See Barton, *Sound*.

$$E_s = -v\left(\frac{\partial p}{\partial v}\right) = \gamma p \text{ (from 49).}$$

$$\therefore \mathscr{V} = \sqrt{\gamma p/\rho} \quad . \quad . \quad . \quad . \quad . \quad (52)$$

Thus if we determine the velocity of sound in the gas we can find γ.

In the case of real gases the relation pv^{γ} = constant does not hold. We can however easily start from the result established for any substance in example (1) in Chap. VII, *viz.*

$$E_s/E_T = \gamma, \quad . \quad . \quad . \quad . \quad (51)$$

whence

$$E_s = -\gamma V\left(\frac{\partial p}{\partial V}\right)_T$$

and

$$\mathscr{V} = \sqrt{-\frac{\gamma V}{\rho}\left(\frac{\partial p}{\partial V}\right)_T} \quad . \quad . \quad . \quad (53)$$

We have to evaluate $\frac{V}{\rho}\left(\frac{\partial p}{\partial V}\right)_T$ from the actual equation of state. Assuming the equation in the form $pV = RT + Bp$, we have

$$\frac{V}{\rho}\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-B)^2}\frac{V}{\rho} = -\frac{RT}{(RT)^2}\frac{p^2V}{\rho}$$

$$= -\frac{1}{RTM}(RT+Bp)^2 = -\frac{RT}{M}\left(1+\frac{Bp}{RT}\right)^2$$

$$\therefore \mathscr{V}^2 = \frac{\gamma RT}{M}\left(1+\frac{Bp}{RT}\right)^2 \quad . \quad . \quad . \quad . \quad (54)$$

Using Berthelot's equation (see Chap. X), in the form

$$pV = RT\left[1+\frac{9}{128}\frac{T_c}{p_c}\frac{p}{T}\left(1-\frac{6T_c^2}{T^2}\right)\right],$$

and comparing with the above we have

$$B = \frac{9}{128}\frac{RT_c}{p_c}\left(1-\frac{6T_c^2}{T^2}\right);$$

and hence

$$\mathscr{V}^2 = \frac{\gamma RT}{M}\left[\ +\frac{9}{128}\frac{T_c}{T}\frac{p}{p_c}\left(1-\frac{6T_c^2}{T^2}\right)\right]^2 \quad . \quad . \quad . \quad (55)$$

For calculating from the experimental results equations (54) and (55) are generally employed.

2·41. We may adopt either of the *two following methods*. The absolute velocity of sound in the gas may be determined or we may compare the velocity with that in another gas (say air) which has been determined accurately by other methods.

For our purpose we discard the large-scale determinations of the velocity of sound in air on account of the various defects inherent in them. A very accurate direct determination of the velocity of sound in air was made by Hebb[1] in 1905 by a method depending on the reflection of sound of known frequency from parabolic mirrors. His mean value after employing all corrections gives 331·41 metres/sec. as the velocity of sound in air at 0°C. and 760 mm. pressure which agrees very well with the best recent value of 331·60 ± 0·05 given by Kneser[2].

Now we must remember that practically all determinations of the velocity of sound in gases have been made in tubes, but the velocity in a tube is not the same as in free space. Corrections have to be applied to reduce this velocity to that in open space. In the foregoing formula the velocity in open space must be substituted.

Dixon[3] has directly determined the velocity of sound in different gases from 15°C. to 1000°C. in a very satisfactory manner. The gas was allowed to traverse a metal pipe about 15 metres in length and 2·5 cm. in diameter. The pipe was coiled spirally and immersed in suitable temperature baths. It was fitted at its two ends with exactly similar aluminium end-pieces, each of which acted as transmitter and receiver in turn. The end-pieces were closed at one end with a thin steel plate, and a hole was made in the wall of the end-pieces and closed by a platinum disc carrying a platinum upright outside. When the steel plate was struck by an electrically controlled hammer, a sound wave started along the tube and when it passed the platinum disc the latter was pushed out, and the upright broke the circuit of a pendulum chronograph. Thus the time sound takes to travel from one disc to the other was automatically recorded and its velocity calculated.

Method based on the Measurement of Wavelength

2·42. Kundt's Tube.—Kundt (1868) first devised an apparatus by means of which he could find the velocity of sound in a gas.

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[1] *Phys. Rev.*, **20**, 89, 1905; **14**, 74, 1919.

[2] *Ann. d. Phys.*, **34**, 665, 1939.

[3] *Proc. Roy. Soc.*, A, **100**, 1, 1921.

This consists simply of a glass tube about 1 metre in length and 3 cm. in diameter. One end of the tube was fitted with a movable stopper, while through the other end passed a loosely-fitting disc carried by a glass or metal-sounding rod which was itself clamped at its centre. Later Kundt employed the double-tube apparatus indicated in Fig. 24. Two tubes A and B are connected by means of the sounding-rod S which is clamped at distances one-quarter of its length from either end. The two rubber corks d, d in the tubes A and B provide the clamping arrangement. The pistons P, P can be moved to and fro to bring the tubes in resonance with the rod S. Throughout the length of each tube is spread some light dust such as lycopodium powder or silica dust. One tube is filled with air and the other with the experimental gas. The sounding-rod S is excited by rubbing it at the centre when the dust is thrown into violent agitation at the antinodes and collects at the nodes. The distance between successive nodes equals half a wavelength, and knowing the frequency of the sound the velocity is easily obtained. The double form of the apparatus is very convenient for comparing the velocity of sound in any gas with that in air for

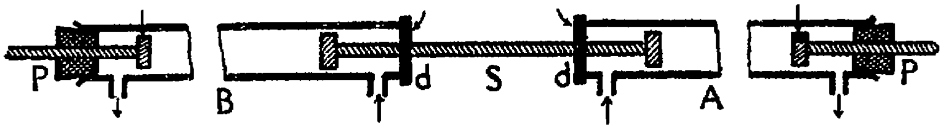

Fig. 24.—Kundt's double-tube apparatus.

$$\mathcal{V}_{gas}/\mathcal{V}_{air} = \lambda_{gas}/\lambda_{air}.$$

From this the velocity in any gas can be easily calculated if the velocity in air is known, and no knowledge of the frequency of sound is necessary.

Various precautions are, however, necessary. The tube and the powder must be perfectly dry. Carefully purified air must be used otherwise correction[1] for the various impurities must be applied. Too much dust should not be used for excess of dust diminishes the velocity. A decrease in the diameter of the tube also diminishes the velocity. Finally, from

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[1] It can be easily shown that for a mixture of perfect gases

$$\frac{p}{\Gamma-1} = \frac{p_1}{\gamma_1-1} + \frac{p_2}{\gamma_2-1},$$

where p_1, p_2 are the partial pressures of these gases, p the total pressure and Γ stands for the ratio C_p/C_v for the mixture.

the velocity in the tube the velocity in open space must be deduced. Though mathematical equations giving the requisite correction have been developed by Helmholtz, Kirchhoff and others, they are not quite adequate.[1] The best method[2] is to express the velocity $\mathcal{V}'$ in the tube as

$$\mathcal{V}'=\mathcal{V}(1-kC),$$

where $\mathcal{V}$=velocity in open space, k=a constant depending on the tube (its radius, thickness, thermal conductivity, surface, frequency of the sound, etc.), C = a factor depending on the gas (its viscosity, density, ratio of specific heats, etc.). Kirchhoff showed that

$$\sqrt{\frac{\eta}{\rho}}\left\{1+\sqrt{\epsilon}\ \left(\frac{\gamma-1}{\sqrt{\gamma}}\right)\right\}, \quad . \quad . \quad . \quad (56)$$

where η=viscosity, ρ=density, γ=ratio of specific heats and $\varepsilon=K/\eta c_v$, K being the thermal conductivity. For k he gives the value $1/(2r\sqrt{\pi n})$ where r is the radius of the tube and n the frequency of the sound waves, but this value is open to criticism.

For air from Hebb's experiments we know $\mathcal{V}$, and by observing $\mathcal{V}'$ and calculating C from (56), k for the tube is determined. This value of k is employed to give $\mathcal{V}$ the velocity in open space for any other gas[3].

Kundt and Warburg (1876) employed this method to determine the velocity of sound in mercury vapour. One of the tubes contained mercury vapour and was heated in an air-bath to about 300°C. The distance between two nodes was measured when the tube cooled. They found $\gamma=1\cdot666$. Ramsay[4] employed this method to find γ for argon but on account of certain difficulties he got a low value. Behn and Geiger[5] improved the apparatus considerably. They dispensed with the sounding-rod and employed a sealed tube containing the experimental gas as the source of sound. This tube was clamped in its middle and was excited like the sounding-rod. The tube should be chosen properly and its length be adjustable so that the contained gas may give resonance with the sound emitted by the rod. This was secured by adding to the ends the requisite number of small metal discs. This sounding tube projected into the comparison tube containing air whose length could also be adjusted. The apparatus was eminently suited for gases at high temperatures. This method was later employed by different investigators particularly by Partington and Shilling.

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[1] See P. S. H. Henry, *Proc. Phys. Soc. Lond.*, **43**, 340, 1931.

[2] See Partington and Shilling: *Specific Heats of Gases*, p. 52.

[3] A different procedure, however, has been adopted by Kaye and Sherratt (*Proc. Roy. Soc.*, **141**, 156, 1933).

[4] *Phil. Trans.*, A, **186**, 228, 1895.

[5] *Verh. d. deuts. phys. Ges.*, **9**, 657, 1907.

2·43. Experiments of Partington and Shilling.—These investigators determined the velocity of sound in various gases up to 1000°C. by a resonance method[1]. Their apparatus is diagrammatically represented in Fig. 25.

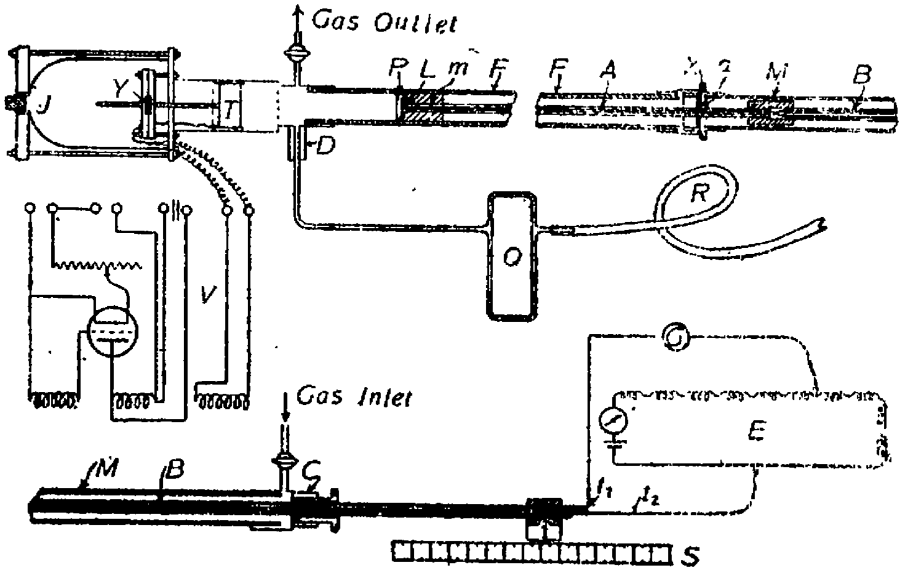

Fig. 25.—Partington and Shilling's Apparatus.

FF is a silica tube 230 cm. long and wound over almost along its entire length with heating coils. To this tube is attached at X a glass tube, MM, 150 cm. long. Inside the former is the piston P of silica carried by the rod A, also of silica. BB is a steel tube joined to A by means of a cork. The tube BB carries a saddle I moving on a millimetre scale, thus the displacement of the piston can be found. Through this tube pass the thermo-couple leads to the potentiometer system E. The other end of the silica tube is closed by a telephone diaphragm T which can be moved by means of the screw Y. This end can be closed gas-tight by means of the bell-jar J. The telephone diaphragm is excited by a valve oscillator V giving a note of frequency 3000. D is a side tube from which a rubber-tube leads to the ear of the experimenter. X is an asbestos plug to prevent radiation of heat to M.

The silica tube is filled with the experimental gas and maintained at the desired temperature. The central tube AB is gradually moved away from D and the successive positions of the saddle I on the millimetre scale corresponding to a maximum sound in D are noted. The successive distances correspond to $\lambda/2$ and knowing the frequency the velocity is determined. The position of T has to be adjusted at different temperatures in order to give maximum sound in D when it will be at a distance $\lambda/2$ from the latter.

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[1] *Trans. Faraday Soc.*, **18**, 386, 1923.

2·44. Cook[1] employed this method to find γ for air and oxygen from 90° to 293°K. His apparatus may be visualized if we imagine the hot air-bath of Kundt and Warburg to be replaced by a long Dewar flask containing liquid air. Similarly, Koch[2] designed a high-pressure apparatus in which one tube was built strong enough to withstand high pressure. The method has also been employed by Sherratt and Griffiths[3] for finding γ for carbon dioxide over the temperature range 0 to 1000°C.

2·45. Results.—In the foregoing pages we have considered the important methods of finding specific heats. Table 4 gives values[4] which best represent the experimental data. We reserve our comments on these values for the next chapter.

2·46. Special Calorimeters.—Various types of calorimeters have been devised for special purposes, *e.g.*, for the measurement of the heat of combustion[5] or explosion, heat of chemical reactions, heat of solution,[6] heat of mixture,[7] heat of dilution[8], heat of absorption[9] or heat evolved by radioactive bodies, etc. etc. Sometimes differential calorimeters are also employed for the measurement of very small quantities of heat. It is not possible to give here even a brief account of these. For a complete account the reader is referred to *Handbuch der Experimental-physik*, Vol. 8, Part I, Chapters III, XIII, XIV and XV. We shall describe here only a few of them.

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[1] *Phys. Rev.*, **23**, 212, 1906.

[2] *Ann. d. Physik.*, **26**, 551, 1907.

[3] *Proc. Roy. Soc.*, A., **156**, 504, 1936.

[4] Taken from *Handbuch der Experimental-physik*, **8**, 33.

[5] Richards, *Jour. Amer. Chem. Soc.*, **42**, 1599, 1922; v. Wartenberg and Husen, *Z. f. angew. Chemie*, **38**, 183, 1925.

[6] Lange and Dürr, *Zeits. f. phys. Chem.*, **118**, 135, 1925; Lipsett, Johnson and Maass, *Jour. Amer. Chem. Soc.*, **49**, 925, 1927.

[7] Randall and Bisson, *Jour. Amer. Chem. Soc.*, **42**, 351, 1920; Lange and Dürr, *Zeits. f. phys. Chem.*, **121**, 364, 1926.

[8] Nernst and Orthmann, *Zeits. f. phys. Chem.*, **135**, 199, 1928.

[9] Von Magnus and Kälberer, *Zeits. f. phys. Chem.*, **125**, 352, 1926.

Table 4.—*Molecular Heats in Calories at* 20° *C. and Atmospheric Pressure.*

Gas	C_p	C_v	$\gamma = \frac{C_p}{C_v}$	Remarks
Argon ..	4·97	2·98	1·666	Monatomic
Helium ..	4·97	2·98	1·666	
Hydrogen ..	6·865	4·88	1·408	Diatomic
Oxygen ..	7·03	5·035	1·396	
Nitrogen ..	6·95	4·955	1·402	
Nitric oxide ..	7·10	5·10	1·39	
Hydrochloric acid	7·04	5·00	1·41	
Carbon monoxide	6·97	4·98	1·40	
Chlorine ..	8·29	6·15	1·35	
Air . ..	6·950	4·955	1·402	
Carbon dioxide	8·83	6·80	1·299	Triatomic
Sulphur dioxide	9·65	7·50	1·29	
Hydrogen sulphide	8·3	6·2	1·34	
Ammonia ..	8·80	6·555	1·315	Polyatomic
Methane ..	8·50	6·50	1·31	
Ethane ..	12·355	10·30	1·20	
Acetylene ..	10·45	8·40	1·24	
Ethylene ..	10·25	8·20	1·25	

Differential Calorimeters or Microcalorimeters.—These have been devised by Steinwehr (1901). Wertenstein[1], Douane, Randall and Bisson[2], Nernst and Orthmann and others. Wertenstein found with its help the amount of heat evolved by a small quantity of radioactive substance. His apparatus is represented diagrammatically in Fig. 26, p. 106.

The iron block A is kept at a constant temperature by a thermoregulator. In it are embedded two Dewar flasks D which are identical in all respects, *viz.*, size, heat capacity, etc. The portions shaded black represent mercury which is used for making good thermal contact. Inside the Dewar flask and separated from it with paraffin, are two vessels G, R which are also absolutely identical. One contains the source giving the heat to be measured while the other contains a heating coil which can be heated to any desired amount by sending a suitable current. Any temperature difference between G and R could be accurately measured with a large number of Cu-constantan thermocouples E, E arranged differentially and connected to a galvanometer. The heating current is varied and adjusted so that there is no deflection in the galvanometer. When it is so adjusted, the quantity of heat evolved by the substance is equal to the electrical energy supplied to the wire.

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[1] *Jour. de phys. et le Radium*, **1**, 126, 1920.

[2] *Jour. Amer. Chem. Soc.*, **42**, 347, 1920.

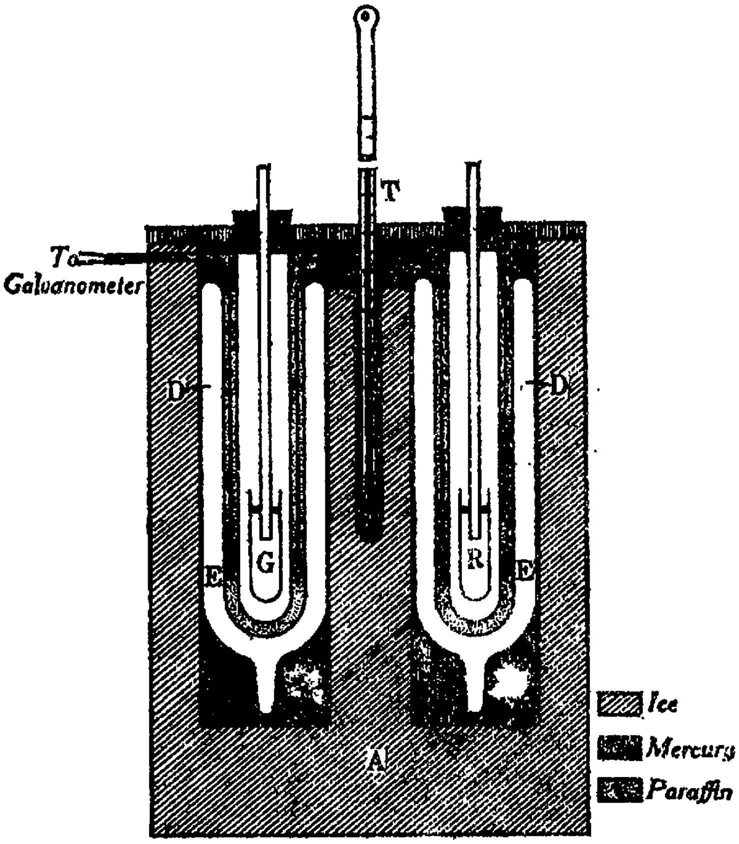

Fig. 26.—Wertenstein's Differential Calorimeter.

Calorimetric Bomb.—For chemical and industrial purposes it is very important to determine the heat of combustion of various substances. This can be easily done with the calorimetric 'bomb' a modern form of which is indicated in Fig. 27. It consists of a stout steel-cylinder A fitted with a cover held down tightly by suitable means. The cover has a milled-head screw valve by means of which the size of the opening k_1 can be varied and the admission of oxygen through the tubes B and C into the bomb can be regulated. Through the centre of the cover but insulated from it passes the wire *i* which is connected to the platinum wire W, the other end of the latter being connected to *e*. There is another similar screw valve for varying the size of the opening k_2 through which gas can go out of the bomb. To enable the bomb to withstand the

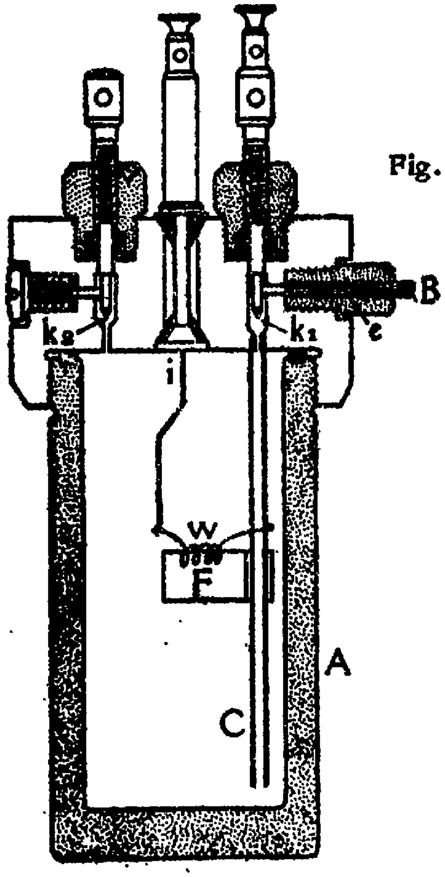

Fig. 27.—The Bomb.

corrosive action of the products of combustion it is plated inside with gold, though platinum would be better. The bomb is enclosed in an ordinary calorimeter such as is used for the method of mixtures. This calorimeter is provided with a stirrer and accurate thermometers. The whole is surrounded by a constant temperature jacket.

To find the heat capacity of the bomb and its accessories a known amount of electrical energy may be spent in the system or a fuel of known calorific value burnt. The former method is adopted in standardising laboratories and the latter in factories. Benzoic acid is most suitable for this calibration. The fuel, if solid, is formed into a small briquette; if liquid, it is soaked in pure cellulose and put in the platinum dish F and ignited. About three times the amount of oxygen just necessary for complete combustion is admitted through B, C. The oxygen is generally employed at a pressure of about 25 atmospheres and at this high pressure the combustion is almost instantaneous.

PROBLEMS

1. Dry air enclosed at 25°C. and atmospheric pressure is suddenly compressed to half its volume. Find (1) the resulting temperature, (2) the resulting pressure. Assume $\gamma=1\cdot40$.

2. In an experiment using the Callendar and Barnes' method, when the rate of flow of water was 11 gm. per minute, the heating current 2 amperes and the difference of potential between the ends of the heating wire 1 volt, the rise of temperature of the water was 2·5°C. On increasing the rate of flow to 25·4 gm. per minute, the heating current to 3 amperes and the potential difference between the ends of the heating wire to 1·51 volts, the rise of temperature of the water was still 2·5°C. Calculate the value of the mechanical equivalent of heat.

3. In a determination of the specific heat at constant pressure by Regnault's method the gas is supplied from a reservoir whose volume is 30 litres at 10°C. The pressure of the gas in the beginning is 6 atmos., and in the end 2 atmos., the temperature remaining constant at 10°C. The gas was heated to 150°C. and led into a calorimeter at 10·0°C. The final temperature of the calorimeter and contents was 31·5°C. and its water equivalent was 210 gm. If the density of the gas is 0·089 gm. per litre at N.T.P., calculate its specific heat at constant pressure.

4. Determine the ratio of the specific heats of air from the following data:—Velocity of sound=34215 cm. per sec. in air at 750 mm. and 17°C.; density of air= 0·00129 gm. per c.c. at N.T.P.; coefficient of expansion of air= 1/273 per °C,; g= 981 cm./sec.^{2}; density of mercury= 13·6 gm. per c.c.

Books Recommended

(1) Glazebrook, *A Dictionary of Applied Physics*, Vol. 1, article on 'Calorimetry'.

(2) Partington and Shilling, *Specific Heats of Gases.*

(3) *Handbuch der Experimental-physik*, Vol. **8**, Part I.

(4) *Handbuch der Physik*, Vol. **10**, Chapter VI.

CHAPTER III

KINETIC THEORY OF MATTER

THE NATURE OF HEAT

3·1. Historical.—In the legends of some ancient nations, it is said that fire was first made for man by some friendly spirit by rubbing together two pieces of stick, *e.g.*, the legend of Prometheus in Greece and of Pururava and Urvasi in the Rig Veda. The legend probably refers to a prehistoric discovery of the art of making fire. But though this way of producing heat by friction clearly indicates the real nature of heat, the early philosophers had no correct notion about it. They formed their ideas of the nature of heat from the observation that heat could pass spontaneously from a hot body to a cold one. Heat was therefore supposed to be a kind of fluid—the caloric fluid filling the interspaces between the molecules of matter. It was further supposed that the body became warmer when caloric was added to it while the removal of caloric produced a cooling.

Various fictitious properties were assigned to this hypothetical fluid. It was supposed to possess no weight, since bodies did not increase in weight on mere heating. Further, it was supposed to be highly elastic, all pervading, indestructible and uncreatable by any process. Temperature was likened to potential or level in hydrostatics. When the body was heated the caloric fluid was supposed to stand at a higher level than when cold. Production of heat by friction was compared to the oozing out of water from a sponge when squeezed. The caloric when thus squeezed out manifested itself as heat.

Doubts on the caloric theory of heat began to be thrown towards the end of the eighteenth century. The earliest philosopher to form a correct idea of the physical nature of heat was Benjamin Thompson *alias* Count Rumford, an American by birth, who being loyal to Great Britain during the American War of Independence, had to flee from his country. He took service under the Elector of Bavaria as superintendent of the artillery. In those days guns were made by casting solid cylindrical pieces and scooping out the inside by means of a boring machine. Rumford[1] observed that apparently an inexhaustible amount of heat could be produced by the friction of the borer with the body of the gun, though the amount of iron scraped was very small. He undertook protracted experiments and found that the amount of heat produced (measured by the raising of water to a high temperature) bore no relation to the amount of iron scraped, contrary to what one would expect on the caloric fluid theory, but was proportional to the amount of motion lost. He therefore rejected the caloric theory and asserted that *Heat is only a kind of Motion. Whenever Motion disappears it reappears as Heat and there is an exact proportionality between the two.* He even made an estimate of the ratio between the energy dissipated and the quantity of heat evolved and his value is not much different from the value now adopted as standard.

In 1799, Sir Humphry Davy in the Royal Institution of London showed that when two pieces of ice were rubbed together water is produced. It was admitted by all that water contained a larger amount of caloric fluid than ice. Now supporters of the caloric theory asserted that heat is generated in friction because the substance produced by friction contains less heat than the original substance. But the substance produced in Davy's experiment (water) contains more heat than ice, hence the caloric theory became untenable. Davy's experiment proved the greatest stumbling block for the caloric theory.

But the valuable work of Rumford and Davy was soon forgotten and it was only about forty years later that the first law of thermodynamics gained general publicity through the researches of Joule in England, Mayer and Helmholtz in Germany, and Colding in Denmark.

3·2. Early Experiments on Mechanical Equivalent of Heat.—In 1840 J. Joule of Manchester began his classical experiments for determining the exact value of the ratio between the work done and heat generated. Heat was produced by churning water contained in a cylinder by means of brass paddles.

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[1] *Phil. Trans.*, 1798.

These could be kept revolving by means of a double thread wound over a solid cylinder and passing over pulleys, and carrying weights at either end. The amount of work done was calculated by observing the height through which the weights fell. The rise in temperature was measured by a mercury thermometer and hence the heat generated could be found. After applying various corrections Joule found that 772 ft.-lbs. of work at Manchester are necessary to raise the temperature of one pound of water through 1°F. In 1878 Joule used a modified form of the apparatus in which the work done was measured by the application of an external couple as in Rowland's experiments (§3·5). The conversion of work into heat was thus established by the experiments of Rumford and Joule.

3·3. The Inverse Phenomenon—Conversion of Heat to Work.—Between the times of Rumford and Joule, the steam-engine had been widely applied for various industrial purposes. As we shall see later, this is one of the many contrivances for the conversion of heat into work. Thus it was fully established that heat and work are mutually convertible and a definite relation exists between the work dissipated and heat generated. These two facts, *viz.*, the possibility of converting work into heat and *vice versa*, and the existence of a definite relation between the two, are expressed by the First Law of Thermodynamics. Mathematically the law may be stated thus[1] :—

If W is the work done in generating an amount of heat H, we have

$$W=JH, \qquad \ldots \ldots \qquad (1)$$

where J is a constant, provided all the work done is spent in producing heat and no portion is wasted by friction, radiation, etc. If H is expressed in calories and W in ergs, $J=4{\cdot}185\times10^7$. The truth of the second statement embodied in the law is amply proved by the fact that the various methods for finding J (§3·4—3·7) yield almost identical values.

3·4. Methods for Determining J.—Various methods[2] have been devised for finding the value of the mechanical equivalent of heat but the method of fluid friction and the electrical method are the only ones capable of yielding accurate values, and hence only these will be considered in detail. There is, however, an ingenious method of calculating the value of J first given by J. R. Mayer. From the theoretical relation $J(C_p - C_v) = R$ (p. 80), he calculated the value of J. Thus for hydrogen $C_p - C_v = 1{\cdot}985$ cal. per mol per °C. (p. 105) and $R = 8{\cdot}314 \times 10^7$ ergs per mol per °C (p. 18). Hence

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[1] For a more formal statement see Chap. V, Sec. 5·12.

[2] An exhaustive list of the older and the newer methods as well as the results deduced therefrom will be found in *Handbuch der Experimentalphysik*, 8, part 1, pp. 30-32, 1929.

$$J = \frac{8{\cdot}314 \times 10^7}{1{\cdot}985} = 4{\cdot}18 \times 10^7 \text{ ergs per calorie.}$$

Certain other methods[1] that have been employed are enumerated below :—

(1) Measurement of heat produced by compressing a gas ——Joule.
(2) Heat produced by percussion——Hirn.
(3) Work done by a steam-engine——Hirn.
(4) Heat developed in a cylinder kept stationary in a rotating magnetic field produced by means of polyphase alternating electric current——Baille and Ferry.

3·5. Rowland's Experiments.—The original experiment of Joule was perfected by Rowland[2], whose apparatus is shown in Fig. 1.

The calorimeter was firmly attached to a vertical shaft *ab* (Fig. 1) to which is fixed a wheel *kl* wound round with a string carrying weights *o*, *p* at either end, the whole being suspended by a torsion wire. The axis of the paddle passed through the bottom of the calorimeter and was attached to the shaft *ef*. The latter could be rotated uniformly by the wheel *g* driven by a steam-engine. The number of revolutions was automatically recorded on a chronograph worked by a screw on the shaft *ef*. The revolution of the paddle at an enormous rate tended to rotate the calorimeter in the same direction on account of fluid friction. This was prevented by the external couple produced by the weights *o*, *p* and the torsion wire. For the purpose of accurately determining the radiation correction a water jacket *tu* surrounded the calorimeter.

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[1] An account of these as well as other methods will also be found in Glazebrook, *A Dictionary of Applied Physics*, **1**, p. 480.

[2] *Proc. Amer. Acad. Arts and Sciences*, **7**, 1880.

The paddle was of a special design. It consisted of a narrow perforated hollow cylinder running along the axis of the calorimeter. To this cylinder were attached four rings, each having eight vanes. Around these were the fixed vanes, consisting of five rows of ten each, which were fixed to the calorimeter. The blades were suitably designed so that the liquid could be vigorously churned. The rise of temperature was measured by a mercury thermometer suspended within the central sieve-like axis of the paddle.

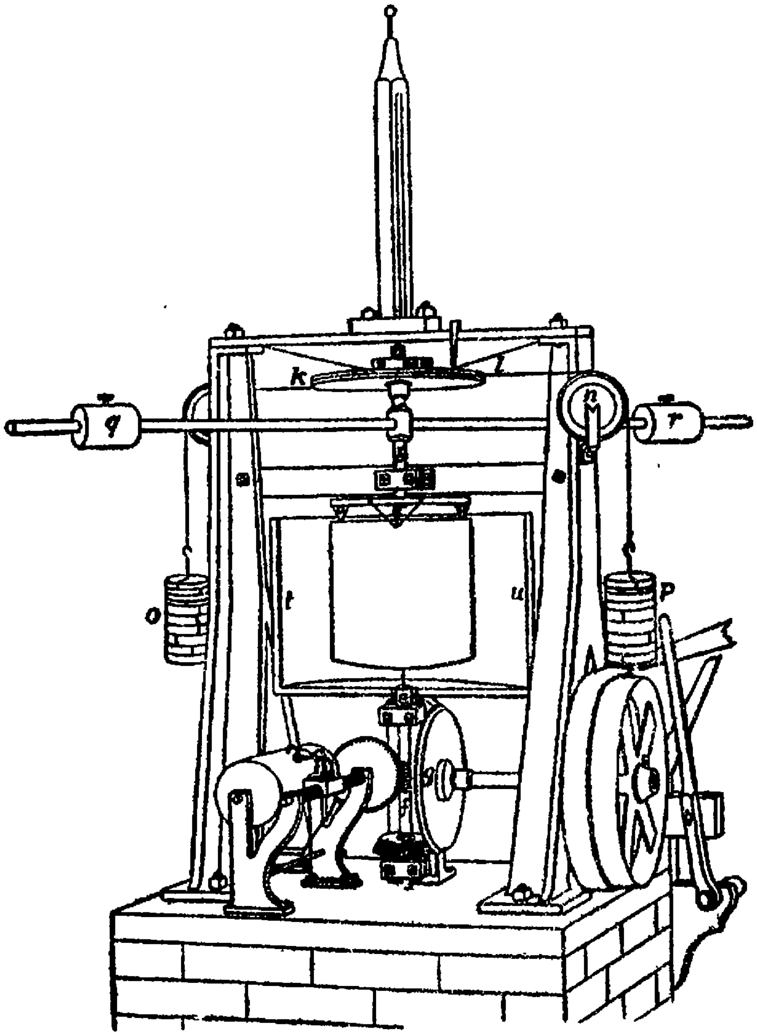

Fig. 1.—Rowland's Apparatus.

If d denotes the diameter of the torsion wheel and mg, mg, the weights suspended, the work W done in n revolutions of the paddle is given by

$$W = \text{couple} \times \text{angle of twist} = mgd \times 2\pi n. \qquad (2)$$

If M denotes the thermal capacity of the calorimeter and its contents, $\delta\theta$ the rise in temperature (corrected for radiation), then the heat produced by friction is equal to $M\delta\theta$, hence

$$J = \frac{2n\pi . mgd}{M\delta\theta}. \qquad (3)$$

If d is in cm. and mg in dynes, J comes out in ergs.

Corrections were applied for the torsional couple, for the weights in air which must be reduced to vacuum, for the expansion of the torsion wheel, etc. Rowland found the mechanical equivalent of the

20° calorie to be $4{\cdot}179 \times 10^7$ ergs. Day[1] recalculated from Rowland's observations by reducing his temperatures to the gas thermometer and found the value $4{\cdot}181 \times 10^7$ ergs for the 20° calorie.

Reynolds and Moorby[2] obtained by a modified apparatus, the value of the mean calorie between 0° and 100°C. to be $4{\cdot}183 \times 10^7$ ergs. More recently Laby and Hercus[3] have employed what is in principle an induction motor, to find J, and obtain the value $J = 4{\cdot}186 \times 10^7$. Their experiments were done with great care and hence we shall describe them in detail.

3·6. Experiments of Laby and Hercus.—These investigators carried out an accurate experimental determination of J by a purely mechanical method, and hence the values obtained by them do not depend upon the accuracy of the values adopted for the electrical units as is the case with the precision experiments of Callendar and Barnes and of Jaeger and Steinwehr. They aimed at an accuracy of 1 in 10,000 and obtained very reliable results. Their apparatus consists of an outer electromagnet, which was rotated at constant speed, and this rotating magnetic field exerted a constant couple on a stator (which was similar in construction to the rotor of an induction motor) supported inside it by a torsion wire carrying a torsion wheel. The stator also acted as a calorimeter of the constant-flow type (as employed by Callendar and Barnes). When the stator was kept stationary by applying an external couple (as in Rowland's experiments), the couple exerted by the rotor on the stator-calorimeter did some work which was measured by the work done against the external couple. All this work is converted into heat whose value was found from the rate of flow and the difference in temperature of inflowing and outflowing water. J could then be easily evaluated.

Fig. 2 shows a section of their induction dynamometer and calorimeter. It was similar to an alternating current induction motor, the chief points of difference being that the squirrel-cage rotor of the motor here becomes the stator-calorimeter and the stator of the motor with its field-windings excited by an alternating current is here replaced by an electromagnet (excited by direct current) which was rotated about a vertical axis and may therefore be called the rotor. The electromagnet NS (Fig. 2) which was similar to the field magnet of a direct-current dynamo, rotated about the vertical axis OZ, the magnet being excited by means of a storage battery of large capacity to which it was connected through slip rings R against which fine copper wire brushes were kept pressed. The rotor was carried on ball-bearings, mounted on a cast-iron framework consisting of a triangular base plate AB and three side members which supported the upper bearings. The base AB which was bolted to a heavy concrete block, was levelled until the axis of the rotor was accurately vertical. This is essential for the clearance space is so small that the rotor may otherwise collide with and wreck the stator. The rotor was belt-driven by a 1 h.p. direct-current motor whose speed was controlled by a centrifugal governor and further regulated by hand. With these devices and by properly selecting the brushes the speed of the motor could be kept fairly constant so that the variations in the couple exerted on the stator were less than 1 in 10,000.

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[1] *Phil. Mag.*, **46**, 1, 1898.

[2] *Phil. Trans.*, 381, 1897.

[3] *Phil. Trans.*, **227**, 63, 1927; *Proc. Phys. Soc.*, **48**, 282, 1936.

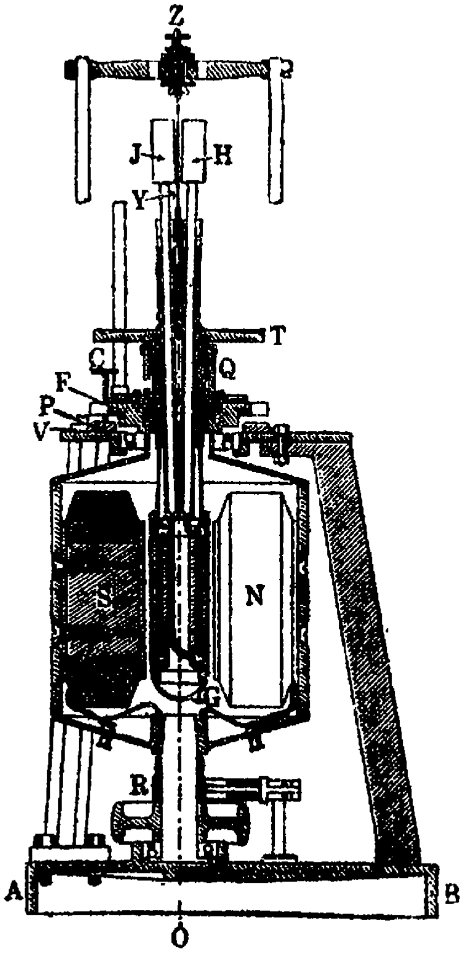

Fig. 2.—A section of the Induction Dynamometer and Calorimeter.

The stator-calorimeter is shown between N and S. It was enclosed in a specially constructed glass vacuum flask G in order to reduce thermal losses as much as possible. The stator was attached to a special type of ball-bearing Q which consisted of two hollow steel cylinders separated by two rings of steel balls. The upper ring of balls was supported by the upper edge of the sleeve. The inner sleeve of the bearing was attached to the torsion wheel T and both were supported by the torsion wire Y whose top had several adjustments. The torsion wheel was 20 cm. in diameter and was made of aluminium copper alloy. To it were attached two tungsten wires, each passing in opposite directions over side wheels (not shown), which were accurately balanced on agate knife-edges, and supporting weights at the other ends. The outer sleeve of the bearing was supported by a flange F, attached to the plate

P by levelling screws C. In addition there were slides V for giving horizontal motion to P. With the help of the slides V and screws C the stator could be levelled and centered, and by supporting in this way the stator is free to rotate except for the couple exerted by the torsion wire and the suspended weights. It is very essential that the axis about which the magnetic field (or rotor) rotates must be parallel to the axis of the stator and have no component of motion parallel to it. It is only when these conditions are fulfilled that the couple acting on the stator will fully correspond to the heat developed. If the magnetic field has a component parallel to the axis of the stator, heat would be generated but there would be no corresponding couple about that axis.

The stator-calorimeter is shown in Fig. 3 and was very similar to the rotor of an induction motor except that copper tubes D were used in place of the usual rods. The inlet water flowed at a constant rate past the resistance thermometer H to the upper annular channel *a*, down fourteen copper tubes D to the lower annular channel *b* and thence through *t* to the outlet thermometer at J. Besides there are thermo-couple junctions at X and K to determine the heat losses. A section of the calorimeter through LM is shown below in the same figure. In this the copper tubes are indicated by thick black circles. The portions of the armature, shown shaded in the figure, were made of stalloy stampings and consequently most of the heat produced by the rotating magnetic field was generated in the copper tubes. As the surface of the copper tubes in contact with the water was large, all the heat developed was taken up by the water. To minimise heat loss the thermometers H and J were enclosed in silvered vacuum jackets. These thermometers were platinum resistance thermometers of Callendar's type, connected differentially so that a single bridge reading gave the difference in temperature between the inflowing and outflowing water. The rate of flow of water was automatically recorded on a chronograph.

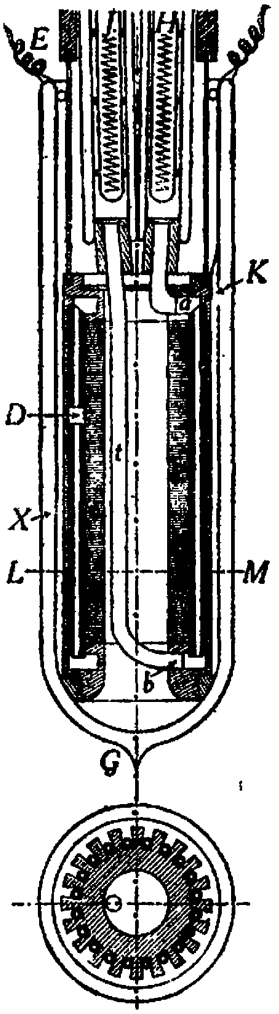

Fig. 3.—The stator-calorimeter.

Neglecting small corrections, the equation for *J* is

$$n\pi mgd = JM\delta\theta,$$

where n is the number of revolutions of rotor, m the total mass suspended corrected for torsion of suspension wire, buoyancy, etc., M the mass of water, d the diameter of torsion wheel plus the diameter of the wire, and $\delta\theta$ the rise in temperature produced. To get accurate values a number of corrections are necessary for the loss of heat through the vacuum flask, heat developed by fluid friction, buoyancy of weights, lack of centering of knife-edge wheels, lack of balance of knife-edge wheels, weight of wire supporting the weights, etc. By taking great precautions they obtained the value

$$1 \text{ calorie at } 16{\cdot}7^\circ\text{C.} = (4{\cdot}1841 \pm 0{\cdot}0001)\times 10^7 \text{ ergs.}$$

Using Callendar's value for the variation of specific heat, this gives

$$15^\circ \text{ calorie} = 4{\cdot}1860\times 10^7 \text{ ergs.}$$

A modification of this method has been suggested by Chowdri and Kothari[1] in which the rotating magnetic field is replaced by a stationary field.

3·7. Electrical Methods.—These methods have already been described in §2·16 – 2·18 in connection with the determination of specific heat of liquids. It is easily seen that if the specific heat of the liquid be known, the same set of equations deduced there will give the value of the mechanical equivalent of heat. If water at 15°C. be taken the specific heat is simply unity, and these methods will give the mechanical equivalent of the 15° calorie. There are two methods:—(1) Rise in temperature method; (2) Steady flow method. The former was employed by Griffiths, Jaeger and Steinwehr and others. Jaeger and Steinwehr, and Osborne, Stimson and Ginnings[2] in particular, obtained very reliable results. The steady-flow method was employed by Callendar and Barnes and others. Callendar and Barnes' experiments were done with great care and skill and are capable of the highest accuracy, but the principal source of uncertainty lies in the value of the electrical units employed.

Laby[3] assumes certain probable values for the electrical units employed by Callendar and Barnes and recalculates from their data the value of the mechanical equivalent of the 20° calorie to be $4{\cdot}1795 \,.\, 10^7$ ergs. This yields $4{\cdot}1845 \,.\, 10^7$ ergs as the equivalent of the 15° calorie.

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[1] *Indian Journ. Phys.*, **14**, 409, 1940.

[2] *Bur. of Stand. J. of Research*, **23**, 243, 1939.

[3] *Proc. Phys. Soc. Lond.*, **38**, 172, 1926.

3·8. Value of the Mechanical Equivalent of Heat.—The determination of the mechanical equivalent of heat has been carried out by a variety of methods by a number of workers. The values obtained by them often vary widely and require to be corrected for certain factors which are subject to considerable uncertainties, *viz.*, the system of thermometry used, the absolute value of electrical units employed, etc. A complete table giving the values obtained by older as well as newer experiments will be found in *Handbuch der Experimentalphysik*, **8**, 30-31. Laby[1] has given a critical discussion of the various important determinations. In table 1 we give the results obtained by the more important and accurate experiments.

Table 1.—Determination of J.

Year.	Observer.	Method.	Corrected value of J in 10^7 ergs for 15° calorie.[2]	Reference.
1880	Rowland ..	Churning with paddle-wheel.	4·1872	*Proc. Amer. Acad.* (7), **15**, 75, 1880.
1902	Callendar and Barnes.	Electrical heating.	4·1845	*Phil. Trans.*, **199**, 55, 149, 1902.
1921	Jaeger and Steinwehr.	Electrical heating.	4·1840	*Ann. d. Physik*, **64**, 305, 1921.
1927	Laby and Hercus.	Work done by a rotating magnetic field.	4·1852	*Phil. Trans.* **227**, 60, 1927.
1939	Osborne, Stimson and Ginnings.	Electrical heating.	4·1858	*J. Bur. Stds.*, **23**, 243, 1939.

Critical Comments. The mercury thermometers employed by Rowland were not previously reduced to the correct gas scale, and hence the temperatures given by him are liable to error. As regards the experiments of Callendar and Barnes it is not possible to say with certainty what the absolute value of the E.M.F. of the Clark cells used by them was. This leaves to us the experiments of Jaeger and Steinwehr, of Osborne, Stimson and Ginnings, and of Laby and Hercus which were all performed with extreme care. From a consideration of all the relevant data Birge[1] adopts the mean value $J = 4 \cdot 1855 \times 10^7$ ergs/cal. which is surely correct to 1 in 1,000 and in all probability to 3 or 4 in 10,000.

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[1] *Loc. cit.*

[2] These values are taken from the following sources:—Laby, *loc. cit*; Birge, *Rev. Mod. Phys.*, **1**, 1, 1929; *Reports on Progress in Physics*, **8**, 109, 1941. The values given by Laby are for 20° calorie, from which the equivalent for 15° calorie has been calculated by assuming Callendar's results, *viz.*, 15° calorie/20° calorie = 1·0012. Some investigators have given the values in abs. joules while others in int. joules. One international joule = 1·00020 abs. joule.

3·9. Heat as Motion of Molecules.—These experiments clearly prove that heat is a kind of motion; the next question is —*motion of what*? The answer was given by Clausius and Krönig in 1857 for the case of gases. They said that heat consists in the motion of molecules or the smallest particles of matter.

Nearly 2500 years ago, Indian savants like Kanad (which means literally *Atom-eater*, a nickname given to the savant by a rival school of philosophy, because he used to bring in too much of atoms in his speculations), the Ionian philosopher Heraclitus (about 500 B.C.), and the Greeks, Leucippus and Democritus, (about 400 B.C.) had pictured matter in the world as made up of minute particles, called atoms, separated by distances. The word 'atom' means 'Indivisible'. They clearly realised that if we go on sub-dividing matter by mechanical or other methods, a stage would be reached when the particle would not be further divisible. The Roman poet, Lucretius, (55 A.D.) drawing his inspiration from earlier writers, wrote a didactic epic poem 'De Rerum Natura' (on the Nature of Things), in which matter was supposed to consist of atoms, which, by their motion, give rise to diverse natural phenomena. But the idea remained a barren speculation throughout the middle ages. In 1738, Daniel Bernouilli of the great Bernouilli family of mathematicians, explained Boyle's Law with the aid of atomic motions (vide §3·14). He may be said to be the actual founder of the quantitative Kinetic Theory of Gases.

About 1807, John Dalton,[2] from his studies of the physical properties of atmospheric and other gases, came to the idea that the ultimate particles of different gases, must have definite weights and sizes. He verified his idea further by an analysis of the data on chemical combination. The history of Dalton's Atomic and Molecular Theories is known to all our readers and no detailed account of it need be given here. Suffice it to say that according to it, all matter is shown to be composed of a large number of molecules, all molecules of the same substance being exactly identical as regards mass, size and chemical properties, but differ in their motion. In the solid and liquid states these molecules are closely packed while in gases they are far apart from one another and move about quite freely.

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[1] *Rev. Mod. Phys.* **13**, 236, 1941; *Reports on Progress in Physics*, **8**, 112, 1941.

[2] See *A new view of the origin of Dalton's Atomic Theory* by Roscoe and Harden, 1896.

Now according to the Kinetic Theory of Matter what we call heat is supposed to consist in the motion of these molecules. The identification of heat with motion of molecules is not a mere hypothesis. It is able to explain and predict natural phenomena and at present there is no doubt that it rests upon solid foundations of truth.

3·10. Growth of the Kinetic Theory.—In the middle of the nineteenth century the kinetic theory of matter, the foundations of which were now firmly established on Dalton's atomic theory, and on the conception that heat is merely molecular motion, received attention from a number of mathematical physicists of the highest ability—Clausius (1822 - 88), Maxwell (1831 - 80) and Boltzmann (1844 - 1906). They were followed by Meyer, van der Waals, Lorentz, Lord Rayleigh and others. The following sections largely **reproduce** their works.

Up to the beginning of the present century, however, the theory had been developed entirely from a mathematical standpoint. The molecules are of course too minute to be seen and there was no direct experimental proof of their actual existence or of their motions. Gradually however much evidence has accumulated in favour of these views, the most important being the Brownian Movement phenomena investigated by Perrin in 1908.

3·11. Physical Evidence of the Existence of Molecules and of their Motion.—(1) The phenomena of diffusion and solution readily suggest the molecular agitation of matter. For example when a cylinder of hydrogen is placed over a cylinder of CO_2, hydrogen is found to diffuse into carbon-dioxide against gravity. Alcohol poured over water should normally remain there as it is lighter, but it gradually diffuses into the entire mass of water. Even gold is found to diffuse into lead when placed in contact.

(2) A gas tends to expand. The moving molecules of the gas tend to fly away and produce this property of expansibility. The rectilinear motion of the molecules is observed in the experiment of Dunoyer.[1] His apparatus consisted of the tube ABC (Fig. 4) divided into three compartments A, B, C by means of the diaphragms D and E. The apparatus is highly evacuated through the side-tube G. The end F containing sodium was heated to about 500° and sodium vapour escaped through circular apertures in D and E and was deposited on H. It was found that this deposit coincided with the geometrical projection of the second hole, formed by joining points in the two holes by straight lines, which proves that the molecules travel in straight lines. This method has been used by a number of workers[2] to produce "molecular rays".

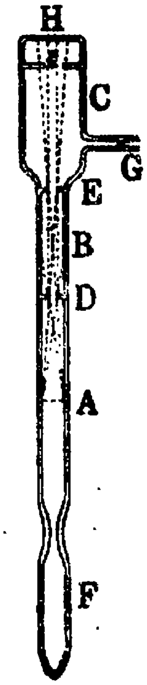

Fig. 4.—Dunoyer's Apparatus.

(3) Phenomena of evaporation and vapour pressure.

(4) The gas laws can be deduced from the kinetic theory (Sec. 3·14). Other results obtained from the kinetic theory as specific heat, Avogadro number, molecular diameter, etc., agree with experimental results or deductions from other branches of Physics.

(5) *Brownian Movement.*—This phenomenon was first discovered by the botanist Brown, in 1827, while observing aqueous suspensions of fine inanimate spores under high power microscope. He found the spores dancing about in the wildest fashion. The phenomenon can be readily observed if a colloidal solution be examined under a high power microscope, or better under an ultra-microscope. The suspended particles under the ultra-micros-

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[1] *Le Radium*, **8**, 142, 1911.

[2] For more information see R. G. J. Fraser, *Molecular Beams* (Methuen and Co.).

cope, appear like stars of light, moving to and fro, rapidly and continuously, in an entirely haphazard fashion. Each particle spins, rises, sinks and rises again. The motion is perpetual and spontaneous. This irregular motion is called the Brownian movement of the particle.

Experiments have shown that the motion of the suspended particles is not due to any chemical or electrical action. The motion becomes more vigorous when the temperature is increased or a less viscous liquid is chosen. It is just perceptible in glycerine and very active in gases. Smaller particles are found to be more agitated than the bigger ones. No two particles are found to execute the same motion, hence the motion cannot be due to any convection or eddy currents.

The discovery of such spontaneous motion, and the fact that the motion is maintained even in viscous liquids without the application of any force was a great puzzle to earlier observers. Gradually, however, it was recognised that the phenomenon can be easily explained if we imagine that the suspended particles are something like buoys in a sea of molecules, and their wild movements[1] are simply due to the impacts of molecules of the liquid from all sides, which give rise to a resultant unbalanced force acting on the particle in a certain direction. The movement becomes more lively at higher temperatures as the molecules then have more energy. It is evident that the forces due to impacts will almost completely balance if the size of the particle is very large but there can be no balance if the size is small.

The theory of the Brownian movement is given in §3·43-3·48. This phenomenon provides a very useful picture of the gaseous state of matter. Though we cannot see the molecules, we can suppose that like the Brownian particles, the gas molecules are in incessant motion in all directions, frequently colliding against one another. Thus the motion of the gas molecules is of the same nature as that of the Brownian particles, only it is much larger. In fact, as we shall see later, all the laws of the kinetic theory of gases are applicable to the Brownian particles, and can be thereby experimentally verified even though the molecules cannot be seen.

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[1] It is evident that when a Brownian particle is thrown upwards as a result of these impacts, its potential energy increases at the expense of the kinetic energy of the adjacent liquid and a local cooling will take place.

During their motion the gas molecules will collide against the walls of the vessel in which they are confined. This gives rise to the phenomenon of pressure which will be described in the next section. The motion is *chaotic*, *i.e.*, the particles move in all possible directions with all velocities. The potential energy due to attraction between the molecules is extremely small, as is shown by Gay-Lussac-Joule experiment, and will be neglected in the first treatment.

3·12. Pressure Exerted by a Perfect Gas.—When such a mass of gas is confined within a vessel, the molecules will frequently collide against the walls and be reflected from them. In this process each molecule delivers a momentum to the walls. From Newton's second law of motion it follows that a pressure will be exerted on the walls which will be simply the aggregate effect produced by the impact of molecules.

To calculate the pressure we shall first make several simplifying assumptions :—

(1) Though the molecules are incessantly colliding against one another, yet in the steady state the collisions do not affect the molecular density in any element of volume of the gas. The molecules do not collect at one place in larger numbers than at another.

(2) Between two collisions a molecule moves in a straight line with uniform velocity. This is because the molecules are material bodies and must obey the laws of motion.

(3) The dimensions[1] of a molecule may be neglected in comparison with the distance traversed by it between two collisions, called its free path. The perfect gas theory treats the molecules as being of infinitesimal size when collisions among them will be negligible. This is particularly so when the gas is highly rarefied.

(4) The time during which a collision lasts is negligible compared with the time required to traverse the free path.

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[1] If we take into account the dimensions of the molecules and the forces of attraction we get van der Waals' equation (Chap. X).

(5) The molecules are supposed to be perfectly elastic[1] hard spheres. Further no appreciable force of attraction or repulsion is supposed to be exerted by them on one another or on the walls, except during an actual collision, *i.e.*, all energy is kinetic. This is approximately so, as shown by Joule's experiment (§2·27).

According to this picture of a perfect gas we find that at any instant there will be molecules moving in all directions with any velocity between 0 and ∞. The direction and the magnitude of the velocity are both distributed at random.

We now proceed to calculate the pressure exerted by such a gas. There are in the main two methods. We may follow the method of general dynamics and write out the equations of motion (Chap. X). Or we may employ the method of collisions. We adopt here the latter method.

Let the velocity of a molecule be denoted by c having the components u, v, w. We have $c^2 = u^2 + v^2 + w^2$. 'c' may vary from 0 to ∞, and u, v, w can each vary from $-\infty$ to $+\infty$. Let us now consider a perfect gas enclosed in a vessel and take the x-axis to be perpendicular to one surface of the vessel. Then a molecule moving with the velocity component u towards the wall collides with the latter. From the principles of conservation of energy and momentum it follows that the molecule after collision has the velocity $-u$. Hence the change in momentum suffered by a single molecule[2] during collision is $2mu$. In the reflection the other components of the velocity suffer no change, hence they contribute nothing to the pressure and can be neglected. Now pressure is equal to the change of momentum suffered by molecules striking unit area of the wall per second, hence it is equal to $2mu$ *multiplied by the number of impacts* delivered on the surface in unit time. The number of impacts on an area δA in time δt must be equal to $n_u u\delta t\delta A$ where n_u is the number of molecules[1] per unit volume having the velocity u. This is because for calculating the pressure, we should consider only those molecules which can reach the surface in time δt and deliver their blows. These must be the molecules which are contained within a cylinder (Fig. 5) whose base AB is of area δA and whose axis DA and vertical height DE are respectively equal to $c\delta t$ and $u\delta t$. Thus its volume is $u\delta t\delta A$ and number of molecules having the velocity u contained in it is $n_u u\delta t\delta A$. Hence p, the pressure on the wall averaged through the time δt or some comparatively long interval of time, is given by the relation

---

[1] The assumption of perfectly elastic collisions, *on the average*, is warranted by the fact that we can convert into work all the heat supplied to a gas. For otherwise addition of heat would increase molecular velocities and hence also the force of collision, and if deformation of molecules results, all heat cannot be converted back to work. The picture here given is essentially that of a monatomic molecule; there will occur deformations of polyatomic molecules accompanied by an increase or decrease of rotational and vibrational energies but on the average there is no net loss or gain of translational energy during collision. Equation (9), however, can be deduced without the assumption of perfectly elastic collision (see Footnote 2 below).

[2] We have assumed here that the molecule on striking the surface bounces off with the same velocity and at the same angle at which it collided. This has been done for the sake of simplicity and is probably not true as shown by Knudsen (§3·50), and is not at all essential to the proof. All that is necessary is that, *on the average*, the molecules should leave the surface with the same energy with which they were incident —an assumption which may be taken to be proved from the experimental

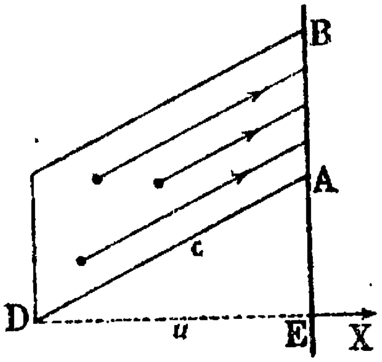

Fig. 5.—
Calculation of pressure.

$$p\delta A\delta t = \sum 2mu \times n_u\, u\delta t\delta A,$$

or

$$p = 2m\sum n_u u^2 \qquad \ldots\ldots \quad (4)$$

The sign of summation has been put because the pressure is caused by all molecules having a positive x-component of velocity, and

---

fact that the walls of a vessel enclosing a gas at a temperature equal to its own do not become heated or cooled. With this assumption a pressure equal to half of that given by (4) will be exerted on the wall in bringing the incident molecules to rest, and an equal pressure is further needed to create the new momentum for restoring the motion of the molecules which may be calculated in the same way as above and will be equal to half of that given by (4), the summation extending over negative values of u. Thus the pressure is again given by (4). In this proof we do not assume the molecules to be hard or spherical and make no postulate regarding the direction or magnitude of the velocity of the molecule after reflection.

[1] It is easy to see that all the molecules cannot have the same speed for even if at any instant all the molecules possess the same speed, collisions at the next moment will augment the velocity of some and diminish that of others.

therefore we should sum for all such molecules. n_u is in general a function of u which was first determined by Maxwell. We may however put

$$\sum_{u=0}^{u=\infty} n_u u^2 = \tfrac{1}{2} n\overline{u^2}, \quad . \quad . \quad . \quad . \quad (5)$$

where $\overline{u^2}$ = mean value of the quantity u^2 for all the molecules and is called the *mean square velocity*, and n the total number of molecules per c.c. We have added the factor $\frac{1}{2}$ because we are summing only for positive values of u, and this number is only $\frac{1}{2}n$ per c.c. Hence equation (4) yields

$$p_x = mn\overline{u^2}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Similarly, the pressures perpendicular to the other sides are

$$p_y = mn\overline{v^2}, \qquad p_z = mn\overline{w^2}.$$

Since observation shows that $p_x = p_y = p_z$ we have

$$\overline{u^2} = \overline{v^2} = \overline{w^2}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This is also consistent with the fact that there is no accumulation of the molecules in any part of the vessel. But

$$\overline{u^2} + \overline{v^2} + \overline{w^2} = \overline{c^2}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $\overline{c^2}$ is the *resultant mean square velocity.*[1] Hence from (7) and (8) we have

$$\overline{u^2} = \tfrac{1}{3}\overline{c^2},$$

and finally (6) yields
$$p = \tfrac{1}{3}nm\overline{c^2}. \quad . \quad . \quad . \quad . \quad (9)$$

But $mn = \rho$, the density of the gas, since n is the number of molecules per c.c. Therefore

$$p = \tfrac{1}{3}\rho\overline{c^2} = \tfrac{2}{3}.\tfrac{1}{2}\rho\overline{c^2} = \tfrac{2}{3}E, \quad . \quad . \quad . \quad (10)$$

where E is the kinetic energy per unit volume. Thus we see that the pressure of a perfect gas is numerically equal to two-thirds of the kinetic energy of translation per unit volume.

In the above we have not considered the possibility that a particle, while approaching a wall, may suffer collision and be turned back. This possibility, however, does not vitiate the argument. It is easily disposed of when we remember the fact that while one particle may be turned back by collision, there will be another corresponding molecule which will be turned in the opposite direction by collision. Without such compensatory processes there can be no balance. In these collisions the molecule gives its whole momentum[1] to the other which by assumption (3) has to traverse exactly the same distance as the first one if there had been no collision. By assumption (4) no time is lost in this collision and hence our calculation holds true for a perfect gas.[2]

---

[1] $\overline{c^2}$ is defined by the relation $\sum n_c c^2 = n\overline{c^2}$ where n_c is the number of molecules having the velocity c and the summation extends over all molecules. Equation (8) can be readily deduced for
$n\overline{c^2} = \sum n_c c^2 = \sum n_c(u^2+v^2+w^2) = \sum n_c u^2 + \sum n_c v^2 + \sum n_c w^2 = n(\overline{u^2}+\overline{v^2}+\overline{w^2})$.

3·13. Root Mean Square Velocity.—Equation (10) enables us to calculate the mean square velocity $\overline{c^2}$ of the molecules of any gas, for $\overline{c^2} = 3p/\rho$. The pressure and density of a gas can be found experimentally and hence $\overline{c^2}$ calculated. To take an example the density of nitrogen at N.T.P. is 0·00125 gm. per c.c. Hence for nitrogen the *root mean square velocity*[3]

$$C = \sqrt{\overline{c^2}} = \sqrt{\frac{3\times76\times13{\cdot}59\times981}{0{\cdot}00125}} = 4{\cdot}93\times10^4 \text{ cm./sec.} \quad . \quad (11)$$

The formula also shows that the molecules of the lightest gas, *viz.*, hydrogen, would move faster than the molecules of any other gas under the same conditions.

3·14. Deduction of Gas Laws.—From the above result we proceed to deduce the laws of perfect gases.

(1) *Avogadro's Law.*—If there are two gases at the same pressure p we have from (9)

$$p = \tfrac{1}{3}\, m_1n_1C_1^2 = \tfrac{1}{3}m_2n_2C_2^2 \quad . \quad . \quad . \quad (12)$$

where the subscripts 1 and 2 refer to the first and the second gas respectively. Further, if the two gases are also at the same temperature we know there will be no transfer of heat (or energy since the two are equivalent by the First Law of Thermodynamics) from one to the other when they are mixed up. On mixing, the two types of molecules will collide against one another and there will be a mutual sharing of energy. Clausius and Maxwell showed purely from dynamical considerations that the condition for no resultant transfer of energy from one type of molecules to the other is that the mean translational energy of molecules of the one type is equal to that of the other.[1] Hence if the two gases are at the same temperature it follows that

---

[1] This result may be easily deduced from the laws of elastic impact (assumption 5).

[2] For more rigorous treatment see §3·33, Problem 3.

[3] C is the square root of the mean square velocity and differs from the mean velocity $\bar{c}$. The relation between C and $\bar{c}$ is given later.

$$\tfrac{1}{2}m_1C_1^2 = \tfrac{1}{2}m_2C_2^2. \quad . \quad . \quad . \quad . \qquad (13)$$

Combining (12) and (13), we get

$$n_1 = n_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

i.e., two gases at the same temperature and pressure contain the same number of molecules per c.c. This is the famous law first discovered by Avogadro.

(2) *Boyle's Law.*—Equation (10) states that the pressure of a gas is directly proportional to its density or inversely proportional to its volume. This is Boyle's Law. This holds provided C^2 remains constant which, as shown above, implies that the temperature remains constant.

(3) *Dalton's Law.*—If a number of gases of densities ρ_1, ρ_2, ρ_3 . . . and mean square velocities C_1^2, C_2^2, C_3^2 . . . . be mixed in the same volume, the resultant pressure p, considering each set of molecules, is given by

$$\begin{aligned} p &= \tfrac{1}{3}\rho_1C_1^2 + \tfrac{1}{3}\rho_2C_2^2 + \tfrac{1}{3}\rho_3C_3^2 + \dots \\ &= p_1 + p_2 + p_3 + \cdot\cdot, \quad . \quad . \quad . \quad . \qquad (15) \end{aligned}$$

i.e., the pressure exerted by the mixture is equal to the sum of the pressures exerted separately by its several components. This is Dalton's law of partial pressures.

3·15. Introduction of Temperature.—If we consider a gramme-molecule of the gas which occupies a volume V, we get from (10),

$$pV = \tfrac{1}{3}MC^2, \quad . \quad . \quad . \quad . \qquad (16)$$

M being the molecular weight. In order to introduce temperature in the foregoing kinetic considerations of a perfect gas we have to make use of the experimental law, *viz.*, $pV = RT$. Hence

$$RT = \tfrac{1}{3}MC^2, \quad C^2 = \frac{3RT}{M}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (17)$$

---

[1] This is a special case of the general theorem of equipartition of energy and will be proved in §3·26 from statistical mechanics. Maxwell proved this translatory equipartition of energy in a less satisfactory but direct way in the manner given in Note 1. For a still simpler proof making use of collisions with the wall see Jeans, *Kinetic Theory of Gases* (1940), pp. 21—23.

Thus C^2 is proportional to the absolute temperature which may thus be considered proportional to the mean kinetic energy of translation of the molecules. This is the kinetic interpretation of temperature. Hence, according to the kinetic theory, the absolute zero of temperature is the one at which the molecules are devoid of all motion. This deduction is, however, not quite justified since the perfect gas state does not hold down to the absolute zero. The interpretation given by classical thermodynamics is somewhat different (Chap. VI) and more reasonable. That does not necessarily require that all motion should cease at the absolute zero. Further, according to the quantum theory the substance may have some energy at the absolute zero which is called the zero-point energy (*Nullpunktsenergie*).

We can put $M=Nm$ where m is the mass of a single molecule and N the number of molecules in a gram-molecule, which is usually called the *Avogadro number*. Further let us put $R/N=k$ where k is known as *Boltzmann's* constant. Then we have

$$p=(N/V)kT=nkT, \quad . \quad . \quad . \quad . \quad (18)$$

where n is the number of molecules per c.c. and is known as Loschmidt's number. Further, from (17)

$$\tfrac{1}{2}N m\overline{c^2}=\tfrac{3}{2}NkT, \quad \tfrac{1}{2}m\overline{c^2}=\tfrac{3}{2}kT; \quad . \quad . \quad . \quad (19)$$

i.e., the mean kinetic energy of translation of one molecule is $\tfrac{3}{2}kT$.

3·16. Distribution of Velocities.—In the previous sections we deduced the gas laws from very general considerations. We assumed that though the particles are incessantly colliding and having their velocities changed constantly in direction as well as in magnitude, we can still talk of a steady state in which n_u, the number of molecules having the velocity component u, cannot have its value changed[1] by collisions. The law which expresses n_u in terms of u and other known quantities is called the law of distribution of velocities and was first arrived at by Maxwell in 1859. Before proceeding to deduce the law we shall explain more fully the nature of this law. It will be noted that such an assembly of molecules is a *statistical* system and the problem of finding the distribution of velocities among the molecules is essentially a statistical problem. We shall therefore illustrate the problem by a simple statistical analogy.

---

[1] This is proved in Note 2 from a detailed consideration of the collision between the molecules.

Suppose in a country the assessing department is required to find out the average income per head of the population. They will proceed somewhat in the following way. They will find out the number of persons whose income lies within different small ranges. For example, they will find out the number of persons whose income lies between 10s. and 11s., between 11s. and 12s. and so on. Instead of a shilling, they may choose a smaller interval, say 6d. Then it can be easily seen that the number of persons whose income lies between 10s. and 10/6s. will be approximately half the number found previously for the range 10s. to 11s. We can generalize by saying that the number whose income lies between x and $x+dx$ is $n_x\,dx$. It should be noted that the number is proportional to the interval chosen (dx). To get the average income they should choose the interval to be as small as possible, say a penny. When this is not possible they will choose a bigger interval but their results will be proportionately inaccurate.

To represent graphically[1] the income of the population they will plot a curve with n_x as ordinate and x as abscissa. The curve will be similar to that given in Fig. 6. This will begin with a minimum at 0, rise to a maximum at some point, and thereafter approach the axis of x, meeting it at a great distance. The curve will have this shape because the number of absolute beggars is very small, and the number of millionaires is also small, while the majority of population have average income.

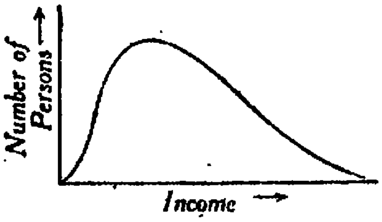

Fig. 6.—Distribution of income among persons.

Let us now return to the problem of a perfect gas enclosed in a vessel. Let it be devoid of all mass motion or convection currents. Following Boltzmann we make the simplifying assumption that in the equilibrium state the gas is in the state of *molecular chaos.* This assumption states that all possible states of motion occur with equal frequency. This really comprises two assumptions[1]—(1) The number n of molecules per c.c. remains constant on the average in course of time in every element of volume throughout the gas ; (2) in every element the molecules have velocities in all directions and have magnitudes which are distributed according to a certain law which does not depend upon the position of the element selected and which will not be modified by collisions.

---

[1] It may be pointed out that for most purposes it is enough to be able to state the number of persons having a certain income and we need not find which person has got what income. Similarly with the molecules. It is quite sufficient to say that so many molecules have so much velocity and so on; which molecule has got what velocity is of little importance and the more so because we do not see the molecules.

We shall now deduce the law of distribution of velocities by the method of probabilities as given by Maxwell[2]. As some of the students are not familiar with the mathematical idea of probability we shall define it here and give some illustrations.[3]

Suppose we toss a coin a large number of times and count the number of times the 'head' or the 'tail' falls uppermost. Common knowledge tells us that if we make a large number of throws, the ratio of the 'heads' to the 'tails' will be one, *i.e.*, the probability of each event is exactly $\frac{1}{2}$. Thus we may define probability in the following terms : if an event can happen in a ways and fail to happen in b ways and each of these ways is equally likely, the probability of its happening is $a/(a+b)$ or, in other words,

$$\text{Probability of an event} = \frac{\text{number of cases in which the event occurs}}{\text{total number of cases}}.$$

Again suppose there are five boys A, B, C, . . .who are desirous of getting a particular red ball. The probability of A getting the red ball is $\frac{1}{5}$. If there is another white ball to be similarly distributed, the probability of A getting it is again $\frac{1}{5}$. The probability that A may get both the balls simultaneously is $\frac{1}{5} \times \frac{1}{5} = \frac{1}{25}$, for there are in all 25 equally likely ways in which the composite event takes place (the red ball may go to any one, say A, then the white ball to any one of the five ; again the red may go to B and then the white to any five; and so on) and the desired event takes place only once. Thus the probability of a composite event is equal to the product of the probabilities of the individual events, provided they are independent.

---

[1] For an analysis of the assumptions underlying the hypothesis of molecular chaos see Jeans, *Dynamical Theory of Gases*, (1925) pp. 59-64. The assumption of molecular chaos seems plausible but is nevertheless open to criticism. However it can be shown from statistical mechanics that in the state of equilibrium this assumption does hold during practically the whole of the time.

[2] Maxwell's original proof is not rigorous. It was subsequently improved by Maxwell himself and by Boltzmann, Jeans and others.

[3] Some more illustrations will be found in Chap. IX.

3·17. Deduction of Maxwell-Boltzmann law.—With this elementary idea of probabilities, we can proceed to deduce Maxwell's law[1]. From the previous analogy it is easily seen that the number of molecules per c.c. having the velocities lying between u and $u+du$ can be denoted as $n_u\,du$. Obviously n_u must be some function of u, say $nf(u)$ where n is the number of molecules per c.c. and $f(u)$ is a function of u to be determined. Then the probability[2] that any molecule selected at random will have velocities lying between u and $u+du$ is $f(u)du$. Maxwell assumed[3] that, as the velocity components u, v, w of a molecule are perpendicular to each other, the distribution of one of these components among the molecules will not depend upon the values of the other components. With this assumption $f(u)$ is independent of v and w. Similarly, the probability for molecules having velocities lying between v and $v+dv$ is $f(v)dv$ and that for velocities between w and $w+dw$ is $f(w)dw$, *the function f being the same on account of isotropy* as regards molecular velocity.

From the theorem of probabilities just established for a composite event, the probability that the velocity components of a molecule shall lie between u and $u+du$, v and $v+dv$, w and $w+dw$ is

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[1] An interesting method of deducing Maxwell's law by disregarding molecular collisions is given by Jeans, *Kinetic Theory of Gases* (1940), pp. 36-38.

[2] $nf(u)du$ denotes the time average of the molecular density in a small element of volume within the specified velocity range. It may happen that at some instant the element of volume contains no molecule at all. Thus if we consider so small a volume that it contains only one molecule on the average, we may regard $f(u)du$ as the fraction of the time for which the elementary volume does contain a molecule. The best view, however, is to regard f as being of the nature of probability so that $f(u)du$ represents the *fractional expectation* of molecules of the specified range in the volume element.

[3] The truth of this assumption is not quite obvious, for the components u, v, w have to satisfy certain conditions, *viz.*, the laws of conservation of energy and momenta for the molecules. Nevertheless the assumption is quite true because these conditions are automatically satisfied for elastic impacts with which we have to deal.

$$f(u)\,f(v)\,f(w)\;du\,dv\,dw,$$

being equal to the product of the individual probabilities. Hence the number of such molecules per c.c. will be

$$n\,f(u)\,f(v)\,f(w)\;du\,dv\,dw.$$

Now let us represent all the molecules in a velocity diagram, with OX, OY, OZ as the coordinate axes (Fig. 7) along which the components u, v, w of the velocity c are respectively measured. Thus a molecule having the velocity components u, v, w will be represented by a point whose coordinates are u, v, w. Such a point is called velocity point. All the molecules whose velocity components lie in the range u, $u+du$, v, $v+dv$, w and $w+dw$ will be contained in the element of volume $du\,dv\,dw$ and the number of such molecules is $nf(u)f(v)f(w)\,dudvdw$. Now these molecules have the resultant velocity c where $c^2=u^2+v^2+w^2$, hence their number must also be equal to $nF(c)\,du\,dv\,dw$, *i.e.*, product of some function of c and the interval $du\,dv\,dw$. It cannot depend upon the inclination of c to the axes for the directions of the axes are quite arbitrary, there being nothing to distinguish one direction from another in a gas at rest. Thus

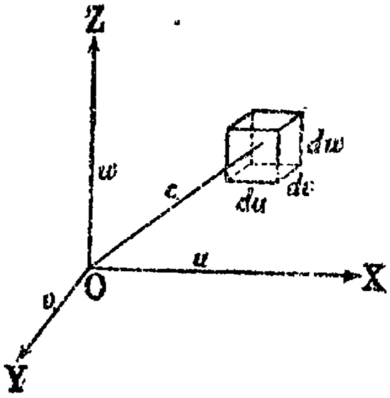

Fig. 7.—Velocity diagram.

$$n\,f(u)f(v)f(w)=nF(c)=n\phi(u^2+v^2+w^2), \quad . \quad . \quad (20)$$

where ϕ denotes some function.

To solve this equation we note that for a fixed value of c, $\phi(c^2)$ is a constant and hence $d[\phi(c^2)]=0$, *i.e.*,

$$d[f(u)f(v)f(w)]=0.$$

$$\therefore f'(u)\,du\,f(v)f(w)+f'(v)\,dv\,f(u)f(w)+f'(w)\,dw\,f(u)f(v)=0.$$

Dividing by $f(u)f(v)f(w)$, we get

$$\frac{f'(u)}{f(u)}du+\frac{f'(v)}{f(v)}dv+\frac{f'(w)}{f(w)}dw=0. \quad . \quad . \quad . \quad (21)$$

Now for fixed values of c, since $u^2+v^2+w^2 = c^2$, the variables du, dv, dw are connected by the relation

$$udu+vdv+wdw = 0. \quad . \quad . \quad . \quad . \quad (22)$$

Combining[1] (21) and (22) by Laplace's method of "undetermined multipliers," we have

$$\left(\frac{f'(u)}{f(u)}+\beta u\right)du+\left(\frac{f'v)}{f(v)}+\beta v\right)dv+\left(\frac{f'(w)}{f(w)}+\beta w\right)dw = 0, \quad (23)$$

where β is a quantity hitherto undetermined. Equation (23) is obtained by multiplying equation (22) by β and adding to (21). The coefficients of the three differentials in (23) must now vanish just as if the differentials du, dv, dw were completely arbitrary. Therefore

$$\frac{f'(u)}{f(u)} = -\beta u.$$

Integrating both sides with respect to u we obtain

$$\log f(u) = -\frac{\beta u^2}{2} + \log a,$$

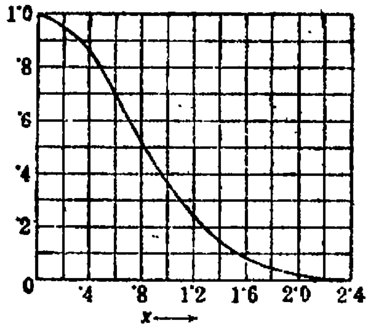

Fig. 8.—The curve e^{-x^2}.

where a is a constant ; or

$$f(u) = ae^{-\frac{1}{2}\beta u^2} = ae^{-bu^2} \quad . \quad . \quad (24)$$

and $f(u)f(v)f(w) = a^3e^{-b(u^2+v^2+w^2)}$. $\quad$ (25)

where a, b are constants.

The distribution law expressed by equation (24) is represented graphically in Fig. 8, where the curve e^{-x^2} is plotted against x. Thus bu^2 has been put equal to x^2. The maximum ordinate corresponds to $u = 0$ and has the value a which has been put equal to 1 in the figure.

3·18. Value of Constants.—To determine a we have, since the total number of molecules per c.c. is n,

$$n\iiint f(u)f(v)f(w)\ du\,dv\,dw = n,$$

---

[1] We might proceed by eliminating dw between (21) and (22) and then utilising the property that du and dv are independent, but the method given in the text is more elegant.

the integration extending from $-\infty$ to $+\infty$ for each variable. Substituting the value of the function, we have

$$\iiint_{-\infty}^{+\infty} a^3 e^{-b(u^2+v^2+w^2)} du\, dv\, dw = 1,$$

whence[1]
$$a^3\left(\frac{\pi}{b}\right)^{\frac{3}{2}} = 1, \quad \text{or} \quad a = \sqrt{\frac{b}{\pi}} \quad . \quad . \quad . \quad . \quad (26)$$

To determine b let us calculate the pressure exerted by the gas, assuming once again that the molecules have no dimensions.

As deduced in §3·12 the pressure p exerted on the wall is given by

$$p = 2m\sum_{0}^{\infty} n_u\, u^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where n_u denotes the number of molecules having the velocity u. But we have shown above that

$$n_u = nae^{-bu^2} = n\sqrt{\frac{b}{\pi}}\, e^{-bu^2}, \quad . \quad . \quad . \quad . \quad . \quad (27)^2$$

from (26). Hence on replacing the sign of summation in (4) by the sign of integration and substituting this value of n_u we get

$$p=2mn\sqrt{\frac{b}{\pi}}\int_0^\infty e^{-bu^2}\, u^2 du = \frac{mn}{2b}$$

from Note 3. But $p = nkT$, hence

$$b = \frac{m}{2kT}. \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Thus the number du of molecules having velocity components lying between u and $u+du$, v and $v+dv$, w and $w+dw$ is[3]

---

[1] See Note 3 for the value of such integrals.

[2] This expression is similar to the well-known Gaussian Law of trial and error. If a marksman fires shots at a target it can be shown that the chance that he strikes at a point having its x coordinate lying between x and $x+dx$ with respect to the target as origin is $\sqrt{K/\pi}\, e^{-Kx^2}\, dx$ where K is a constant which measures the skill of the marksman. Thus we may imagine Maxwell's law to be arrived at by molecules aiming at zero for each velocity component.

[3] Sometimes the relation is expressed in terms of h where $h = 1/(2kT)$, or in terms of α where α is the most probable speed (§ 3·20) and is equal to $\sqrt{(2kT/m)} = 1/\sqrt{b}$.

$$dn = n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m}{2}\left(\frac{u^2+v^2+w^2}{kT}\right)} du\,dv\,dw \quad . \quad . \quad (29)$$

This is Maxwell's distribution law.

From this expression we can deduce the number of molecules having velocities lying between c and $c+dc$. We have

$$u^2+v^2+w^2 = c^2.$$

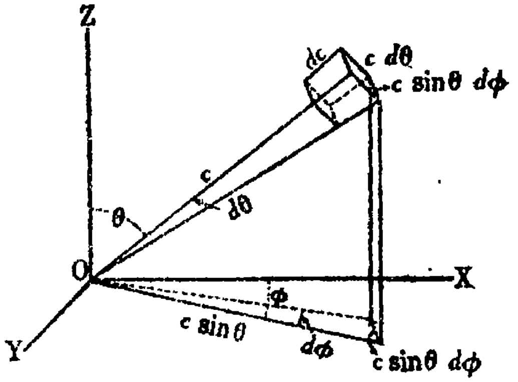

Fig. 9.—Element of volume in spherical coordinates.

Further $du\,dv\,dw$ represents an element of volume in the velocity space and in its place we must substitute the total volume in the velocity space lying between the magnitudes c and $c+dc$ for the resultant velocity. In spherical polar coordinates (r, θ, ϕ) the element of volume is written as $dc.\,cd\theta.c \sin\theta\, d\phi$ (see Fig. 9) and hence this expression must be substituted for $du\,dv\,dw$ in (29) in order to find the number of molecules having velocities lying between c, $c+dc$, θ, $\theta+d\theta$, and ϕ, $\phi+d\phi$. To find the total number of molecules having the velocity lying between c and $c+dc$ we have to integrate this expression for all possible values of θ and ϕ. Thus

$$dn = na^3e^{-bc^2}c^2dc\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta,$$

$$= 4\pi n\, a^3e^{-bc^2}\, c^2dc. \quad . \quad . \quad . \quad . \quad . \quad (30)$$

A slight transformation (putting $bc^2 = x^2$) shows that the number $dn = 4n\pi^{-\frac{1}{2}}x^2\, e^{-x^2}\, dx$ which helps us to represent the law graphically. Let us plot the function $y = 4\pi^{-\frac{1}{2}}\, e^{-x^2}x^2$ against x (Fig. 10). Then the number dn of molecules whose speed lies between x and $x+dx$ is proportional to the shaded area. The ordinate y gives the number of molecules possessing a speed corresponding to x, and from the curve it is obvious that the probability corresponding to $x=1$ is greatest, while it is considerably less for $x=2$ or $x=\frac{1}{2}$. Hence we can approximately treat the whole gas as endowed with the most probable velocity.

Equation (30) clearly shows that there will be molecules of all velocities between 0 to ∞. A simple consequence of this is that those molecules which have got a velocity greater than the velocity of escape c_0 from the planet, will leave the planet's atmosphere. This velocity of escape is given by the relation $c_0{}^2 = 2gr_0$ where g is the gravity at the surface of the planet and r_0 the radius of the planet, and is found to be about 11 kilometres per second for the earth and 2·4 kilometres for the moon. This accounts for the loss of planetary atmospheres and

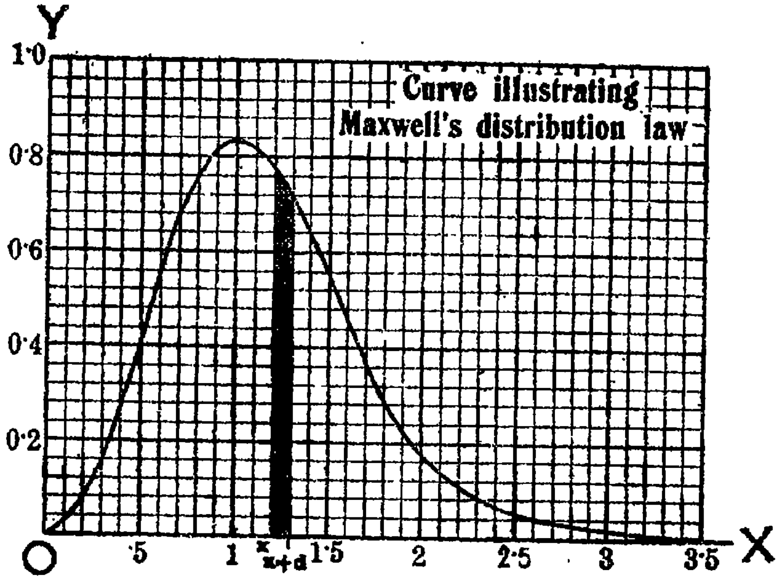

Fig. 10.—Curve illustrating Maxwell's Law.

explains why the atmosphere of the moon is so rarefied. Equation (0) shows that the loss will be much greater at higher temperatures and for lighter gases since $b = m/2kT$.

Exercise.—Show that the fraction of the molecules whose kinetic energy lies in the range ϵ and $\epsilon+d\epsilon$ is

$$f(\epsilon)d\epsilon = \frac{2\sqrt{\epsilon}}{\sqrt{\pi}(kT)^{3/2}}\, e^{-\epsilon/kT}\, d\epsilon.$$

3·19. Comments.—The above is Maxwell's original[1] proof and is based on the assumption that the velocity coordinates are independent. It is on that account more or less open to objection.[2]

On account of this defect Maxwell attempted a second proof by the method of collisions which was carried to completion by Boltzmann. There are two distinct methods of deducing the law :—

(*i*) The method of collisions developed by Maxwell and Boltzmann for certain simple cases. This method gives a lively idea of the processes at work in a gas and is therefore considered at length in Note 2, but is hardly better from the standpoint of strict logic as it assumes that there is no correlation between the velocity and position of a molecule.

---

[1] Maxwell, *Collected Works*, Vol. 1, p. 380; *Phil. Mag.* **19**, 31, 1860.

[2] As Boltzmann has pointed out this deduction cannot be rigorous, for this would hold even if no impacts between the molecules took place. This is impossible.

(*ii*) The method of statistical mechanics developed by Maxwell, Boltzmann, Gibbs, Jeans and others. This is quite free from objection and is applicable to all cases. It will be given in Chap. IX.

3·20. Average Velocities.—We must distinguish between two velocities, the square root C of the mean square velocity, and the mean velocity $\bar{c}$. The former is such that its square is the average of the squares of the velocities of the molecules. Thus[1]

$$C^2 = \bar{c}^2 = \frac{1}{n}\int_0^\infty c^2 dn = \frac{3kT}{m}. \quad . \quad . \quad . \quad (31)$$

The mean speed of molecules is

$$\bar{c} = \frac{1}{n}\int_0^\infty c\, dn = \sqrt{\frac{8kT}{m\pi}}. \quad . \quad . \quad . \quad (32)$$

$$\therefore \frac{\bar{c}}{C} = \sqrt{\frac{8}{3\pi}} = 0{\cdot}921. \quad . \quad . \quad . \quad . \quad (33)$$

The most probable velocity α is that value of c for which n_c the number of molecules with velocity c is maximum. Hence for such value of c, $dn_c/dc = 0$. This relation gives α. Substituting for n_c we get

$$\alpha = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2}{3}}\, C. \quad . \quad . \quad . \quad . \quad (34)$$

Exercise.—Show that the root mean square value of the cartesian component u of the molecular velocity is equal to $\sqrt{p/\rho}$, *i.e.*, Newton's value for the velocity of sound in the gas.

3·21. Experimental Verification of Maxwell's Law.—In the foregoing we have proved Maxwell's law for a gas but it can be shown from statistical mechanics that, at least to a first approximation, the law is equally applicable to the molecules of liquids and to the atoms of solids also.[2] Till 1920, however, there was no direct experimental evidence in support of Maxwell's law of distribution, but a large amount of indirect evidence was available which almost conclusively established the truth of the law. As most of these do not fall directly within the scope of Heat, we shall give here only a brief idea of these experiments.

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[1] dn denotes the number of molecules having velocities lying between c and $c+dc$ and may be written $n_c dc$.

[2] See however Born and Green, *Proc. Roy. Soc. Lond.*, **188**, 10, 1947.

(a) *From the finite breadth of spectral lines.*—Theoretically every monochromatic beam of light should be represented by a line without breadth, but in actual practice every spectral line is found to possess some finite breadth extending over some range in frequency or wavelength. But why does the line emitted by the radiant atom not correspond to one single frequency and is spread about some mean value of the frequency? Schönrock explained the phenomenon as follows:—

If all the atoms were stationary, the light emitted would possess a single frequency and in spectrum photographs it would be represented by a line without breadth (geometric line), but it is clear that no radiating atom in any source of light, be it an arc or a discharge tube, is absolutely at rest. It is on the other hand moving in all directions with all possible velocities. So if the frequency of light emitted by the stationary atom be ν_0, that emitted by an atom moving towards the observer is changed by Döppler effect to $\nu_0(1+v/c)$ where v is the component of the velocity in the line of sight. The intensity of the spectral line at the distance $\triangle\nu = \nu_0 \, v/c$ from the centre of the line will be proportional to the number of particles having the velocity v and an examination of the variation of intensity along the breadth of the line therefore gives us a direct measure of the fraction of the number of molecules possessing the velocity v and thus leads to an experimental test of Maxwell's Law. A more detailed account will be found in Note 4.

(b) *From emission of electrons by heated filaments* (*O. W. Richardson*).—When a metallic wire is heated to a sufficiently high temperature, it is found to emit electrons. According to Richardson, the electrons are present in the interspaces between atoms as a free gas, possessing all velocities between 0 and ∞, and obeying some law of distribution. He planned a series of experiments to find out the nature of the law and concluded that for the emitted electrons the distribution law was Maxwellian. For details see O. W. Richardson, *Emission of Electricity from Hot Bodies*.

3·22. Direct Experimental Proof of Maxwell's law.—The first direct experimental proof of Maxwell's law was attempted by O. Stern[1], and continued by a number of other workers.[2] In these the molecular ray method first given by Dunoyer (§3·11) was employed. The principles employed in these experiments are essentially similar hence we shall describe only a few of them.

Fig. 11 explains the principle of Stern's experiment. A platinum wire L coated with silver (represented perpendicular to the plane of the paper in the figure), is heated by an electric current when it emits atomic silver in all directions. The slits S_1 and S_2, which are parallel to the wire, define a stream of silver which condenses on the plate P. The whole system is enclosed in a glass vessel which is highly evacuated so that silver atoms do not suffer any collision in the space. The slits S_1 and S_2 as well as P are rotated together as a rigid system about the wire as axis. With the plate at rest the stream traverses along LA and forms a deposit at A, but when this system is rotating at a high speed, say clockwise, the deposit will be formed at some point above A, say at B. Faster moving molecules will condense nearer to A than the slow ones, and thus a velocity spectrum of silver will be obtained. If the relative intensity of the deposit be measured with a microphotometer, the ratio of the number of molecules with different velocities can be deduced and the Maxwellian law verified.

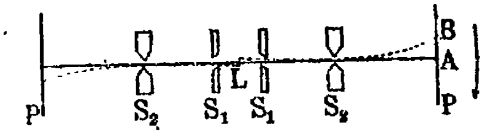

Fig. 11.—Illustration of the Principle of Stern's experiment.

The results obtained by Stern were however not quite satisfactory on account of the difficulty in retaining the vacuum because the spindle of the rotating system had to project outside the vessel for the purpose of coupling it to the driving motor. The dispersion was small and only the distance between the two maxima deposits, obtained by reversing the direction of rotation could be measured. This was 0·7 mm. at the speed of 150 r.p.m. and the Maxwellian law was thereby verified within about 15 per cent.

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[1] *Zeits. f. Physik*, **2**, 49, 1920; **3**, 417, 1920; *Phys. Zeits.*, **21**, 582, 1920.

[2] See the following papers :—Costa, Smyth and Compton, *Phys. Rev.*, **30**, 349, 1927 ; Eldridge, *Phys. Rev.*, **30**, 931, 1927; Zartman, *Phys. Rev.*, **37**, 383, 1931; Estermann, Frisch and Stern, *Zeits. f. Physik*, **73**, 348, 1931; Ko, *Jour. Franklin Inst.*, **217**, 173, 1934.

This difficulty was overcome by Costa, Smyth and K. T. Compton, and by Eldridge by using an induction motor which being actuated by induction currents can be placed entirely in vacuum; while Zartman actually placed his driving motor, which was an ordinary electric motor, also in vacuum. In 1927 Hall designed a new and more sensitive form of the apparatus which has been employed by Zartman. We describe below the experiment of Zartman.

Fig. 12 shows his apparatus diagrammatically. The experimental substance (bismuth) was contained in the steel crucible A which was heated by radiation from a 300 watt tungsten lamp filament F. The substance was thus heated and vaporised, and the vapour passed through the channel in the neck to the slit S_1, 0·05 mm. by 10 mm. in size, there escaping as a molecular beam. The temperature of the crucible was measured with the help of two thermocouples fastened at D and the crucible itself was fastened to the sliding base B which could be so adjusted that the defining slit S_2, 0·6 mm. by 10 mm., was directly above S_1. A shutter M magnetically operated from outside, was used to interrupt the beam. Above S_2 was a knife-edge slit S_3, 0·6 mm. wide, cut into the rim of the cylinder C, 10 cm. in diameter. The cylinder was mounted on the high speed spindle J of an internal grinder whose speed was determined by the stroboscopic method. The grinder consisted of a motor to which the spindle was connected by a driving belt. The motor armature had a speed of 10,000 r.p.m. and the spindle 30,000 r.p.m. All the bearings were lubricated by a vacuum pump oil which was made sufficiently non-volatile so that a

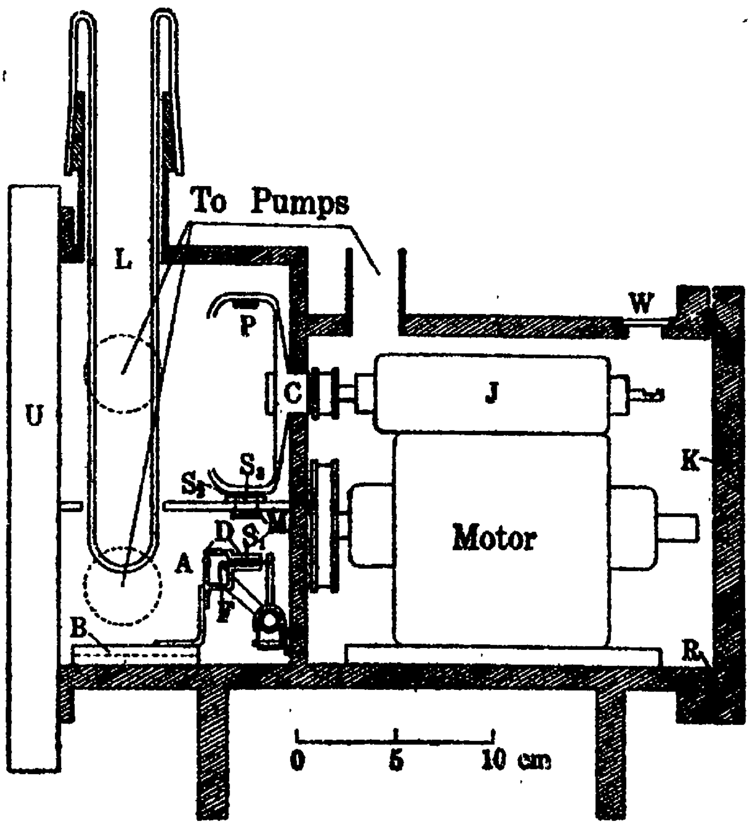

Fig. 12.—Zartman's apparatus for verifying Maxwell's Law.

pressure of less than 10^{-4} mm. of mercury could be obtained in the motor compartment by continual pumping.

The entire assembly was enclosed in a phosphor-bronze housing which was divided into three compartments, a motor, a cylinder and a crucible compartment each of which was connected to a vacuum pump. With the help of the glass tube L which was filled with liquid air, a pressure of less than 10^{-5} mm. of mercury could be maintained in the cylinder and crucible compartments. The deposits were received on a thin glass plate P which exactly fitted the inner surface of the cylinder. For the proper condensation of bismuth molecules on the glass plate at room temperature, it was necessary to deposit a thin uniform layer of bismuth on it by placing it in a suitably designed 'initial depositing' apparatus.

In carrying out an experiment the plate was first kept stationary and exposed to the molecular beam for 20 seconds. It was then removed and a microphotometer record obtained of the density of the initial deposit and location of the zero mark. The plate was again fixed to the cylinder and the latter rotated at a constant speed. The plate was exposed for periods ranging from eight to twenty-two hours and then removed and photometered. Then the two photometer curves were superimposed and the density of deposit due to velocity distribution was measured.

The theory of the experiment is as follows :—The molecules leaving the slit S_3 with the velocity c will be deposited at a distance s from P, the place of deposition when the cylinder is kept stationary, such that

$$s = \frac{\pi n d^2}{c} = \frac{A}{c}, \qquad \ldots \qquad \ldots \qquad (35)$$

where n is the number of revolutions of the cylinder per second and d its diameter. Now the molecules in the emitted beam are not in equilibrium and do not follow Maxwell's law, but those within the enclosure do so. The number passing through the slit per second depends on the size of the opening, the shape of the enclosure, the speed of the molecules and the number dn of molecules in the enclosure having the velocity lying between c and $c+dc$. Hence dn_1 the number of molecules in the emitted beam having the velocity lying between c and $c+dc$ can be denoted by

$$dn_1 = K.c.dn = K.\ 4n\pi a^3\, e^{-bc^2}\, c^3\, dc, \qquad . \qquad . \qquad (36)$$

where K is some constant and is given by

$$n_1 = \int_{c=0}^{c=\infty} dn_1 = \int_0^{\infty} K.\ 4n\pi a^3 e^{-bc} \quad c^3\, dc,$$

n_1 being the total number of molecules in the emitted beam. Hence

$$dn_1 = 2b^2n_1\, e^{-bc^2}\, c^3 dc. \quad . \quad . \quad . \quad . \quad (37)$$

These molecules will be spread over the length lying between s and $s-ds$ where the relation between s and c is given by (35). Hence the intensity I of the deposit for molecules of velocity c at a distance s is given by

$$I = \frac{dn_1}{ds} = \frac{2n_1b^2}{A}\, e^{bc^2}c^5 = \frac{2n^1}{s_a}\left(\frac{s_a}{s}\right)^5\, e^{-(s_a/s)^2} \quad . \quad . \quad (38)$$

where s_σ represents the displacement for molecules having the most probable velocity $\alpha = 1/\sqrt{b}$ and is therefore a constant equal to $\pi nd^2\sqrt{b}$. Actually the central patch has a finite width, say $2a$, and we must take this into account. Thus put $n_1 = I_0\, dx$ where dx is a small width of deposit in the central patch of intensity I_0, and then integrate (38) for values of x from $s-a$ to $s+a$. This yields

$$I = I_0\left[e^{-[s_a/(s+a)]^2}\left\{\left(\frac{s_a}{s+a}\right)^2 + 1\right\} - e^{-[s_a/(s-a)]^2}\left\{\left(\frac{s_a}{s-a}\right)^2 + 1\right\}\right],$$

where the distance $s\alpha$ is measured from the middle point of the central patch.

The results obtained by Zartman are shown in Fig. 13 where the ordinates represent the intensity of deposit and the abscissa the displacement s in cm. from the zero mark or the velocity of the corresponding molecules. The circles and crosses denote the observed results while the full line curves denote the theoretical distribution on the basis of Maxwell's law, assuming the composition of the vapour to be 40 per cent Bi and 60 per cent Bi_2. For curve I, $n = 120{\cdot}7$ r. p. s. and for curve II, $n = 241{\cdot}4$ r. p. s. while the temperature is 851°C. The agreement is seen to be very close thus confirming Maxwell's law.

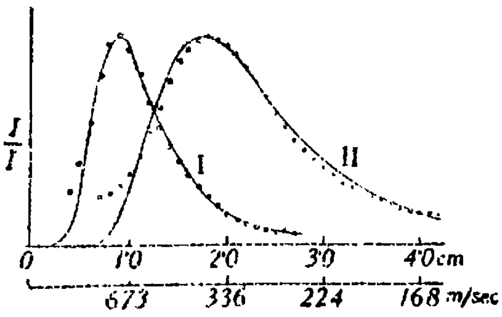

Fig. 13.—Curve showing comparison of experimental results with theory.

It will be seen that the difficulty in verifying Maxwell's law for bismuth vapour is really due to the uncertainty in the molecular composition of the vapour. Unfortunately bismuth evaporates partly as Bi and partly as Bi_2 and probably even slightly as Bi_3. Ko's main object therefore was the determination of the molecular composition of bismuth vapour and he found that the observed deposit agreed with the Maxwellian distribution at the oven temperature on the assumption that the beam contained 44 per cent Bi, 54 per cent Bi_2 and 2 per cent. Bi_3.

A somewhat different method of sorting out the atoms was proposed by Stern[1] which resembles the toothed wheel arrangement used by Fizeau for measuring the velocity of light. Costa, Smyth and Compton and later Eldridge tried to construct an apparatus on this principle but the constructional details were not satisfactory. Eldridge worked with cadmium vapour at 400°C. and interposed between the oven and the receiving plate a system of radially slotted discs mounted on the rotor of an induction motor. These discs acted as a sort of velocity filter so that in any run molecules of different velocities were deposited on the glass plate at different distances from the unshifted line. The principle therefore is really not that of Fizeau's toothed wheel (velocity filter method) but is more analogous to that employed by Zartman (velocity spectrum method), and the accuracy of the experimental arrangement is low as he did not use two similar slits. An apparatus on the toothed-wheel model was successfully constructed by Lammert[2]. Its principle is explained in Fig. 14.

The oven O contains mercury vapour which issues out of the slit S_1. The slit S_2 serves to limit the emerging mercury atoms to a parallel beam moving in the direction S_1S_2. The moving atoms encounter in succession two wheels W_1, W_2 so mounted that they rotate together, and each wheel contains a slit of the same width as the slits S_1, S_2 but the slit in W_2 is not parallel to that in W_1 but is set at an angle of about 2° behind that in W_1. When the wheels W_1 and W_2 are rapidly rotating together, once in each rotation the entire beam of molecules passes through the slit in W_1 and strikes W_2 but only such molecules as have the requisite speed to traverse the distance W_1 W_2 in the time that the wheel W_2 turns through an angle of 2° are able to pass through the slit in W_2 and get deposited on the plate P.

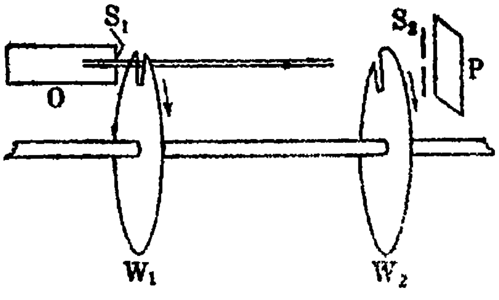

Fig. 14.—Principle of Lammert's velocity filter method.

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[1] *Zeits. f. Physik*, **39**, 751, 1926. [2] *Zeits. f. Physik*, **56**, 244, 1929.

This enables us to separate molecules of a particular speed in the beam and find their number by measuring the intensity of deposit on the plate. By changing the speed of rotation molecules of a different speed can be registered on the screen and their number determined. In the actual experiment the wheel had 50 teeth and thus formed 50 slits. On account of the appreciable width of the slit molecules of a fairly broad range of velocities, rather than of a single velocity, reached the plate. Lammert determined experimentally the fractional number of molecules lying in these different velocity ranges and found that Maxwell's law was obeyed accurately.

In the case of electrically charged atoms a magnetic field has been employed for sorting out atoms of different velocities. These charged atoms traverse a magnetic field and have their paths curved, the radius of curvature being proportional to the speed of the atom. The method has been utilised by Cohen and Ellett[1] for various alkali metals and by Meissner and Scheffers[2] for lithium and potassium.

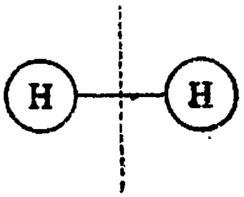

Fig. 15—The H_2 molecule.

3·23. Particles having Degrees of Freedom other than Translational.—In the foregoing we supposed that the molecules have only motions of translation. This is true only when the particles composing a gas are monatomic. But in general only few gases consist of monatomic molecules; most molecules are diatomic or polyatomic. In such cases the motion of the molecule cannot be wholly translational but may consist of other kinds. For example if we take the H_2 molecule, we may suppose that it is formed by two atoms at a certain distance from each other (Fig. 15), the atoms being held together by forces of attraction. Dynamics shows that such a system cannot be stable unless the particles execute a rotatory motion about the common centre of gravity, the centrifugal force due to rotation being equal to the force of attraction. So we conclude that every polyatomic molecule not only moves as a whole, but also rotates about an axis passing through the centre of gravity of the molecule. In the case of H_2 the energy of rotation is given by

$$E_r = \tfrac{1}{2} I \left(\omega_1^2 + \omega_2^2\right), \qquad . \quad . \quad . \quad . \quad (39)$$

where I is the moment of inertia of the molecule and ω_1, ω_2 are the velocities of rotation about the two axes perpendicular to the line joining the two atoms. In general, the rotational energy of a rigid molecule can be written in the form

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[1] *Phys. Rev.*, **52**, 502, 1937.

[2] *Phys. Zeits.*, **34**, 173, 1933.

$$E_r = \tfrac{1}{2}(I_1\omega_1{}^2+I_2\omega_2{}^2+I_3\omega_3{}^2), \quad . \quad . \quad . \quad (40)$$

where ω_1, ω_2, ω_3 are the components of the angular velocity in the directions of the three principal axes and I_1, I_2, I_3 are the moments of inertia about those axes. For diatomic molecules the rotation about the line joining the two atoms produces no new orientation and carries no energy as the moment of inertia about this axis vanishes since the two atoms are supposed to be points situated on the axis.

Besides the energy of rotation, the atoms in the molecule can vibrate or oscillate along the line joining them. This gives rise to extra terms in the total energy. For small oscillations, assuming simple harmonic mode of vibration, this extra energy is given by $E_0 = \frac{1}{2}m\dot{x}^2+\frac{1}{2}\mu x^2$ in the case of a diatomic molecule where m is the reduced mass and is equal to $m_1m_2/(m_1+m_2)$, m_1 and m_2 being the masses of the two atoms, and x is the increase in the distance between the two atoms over their equilibrium distance.

32·4. Degrees of Freedom.—The idea of degrees of freedom may now be introduced. Supposing we watch an ant constrained to move along a straight line, it has then only one degree of freedom and its energy is given by $\frac{1}{2}m\dot{x}^2$. If it is allowed to move in a plane the energy is given by $\frac{1}{2}m\dot{x}^2+\frac{1}{2}m\dot{y}^2$. An ant cannot have more than two degrees of freedom, but a bee which is capable of flying has three degrees of freedom, all of translation. Thus a material particle, supposed to be a point, can have at most three degrees of freedom. A rigid body can, however, not only move but also rotate about any axis passing through itself. The most general kind of rotatory motion can be resolved analytically into rotations of the body about any three mutually perpendicular axes through any point fixed in itself. Hence the position of the body can be completely fixed if we know the three coordinates of the centre of gravity and the three angles to determine the orientation of the body. Thus the degrees of freedom contributed by rotation are three. If an axis is fixed as in the case of a wheel, then it has got only one degree of freedom of rotation because it can rotate about one axis only. We may now define the term '*degrees of freedom*'. The total number of independent quantities which are necessary to specify the configuration of any dynamical system is called the number of *degrees of freedom*[1] of the system. This number depends upon the capacities for motion of the system and not on the motions; it is determined solely by the geometrical and not the mechanical properties of the system. Thus an atom considered as a point, which is the usual practice, has three degrees of freedom; considered as a rigid sphere it has six degrees of freedom. As explained in the previous section, a diatomic molecule will have five degrees of freedom, three of translation and two of rotation if the distance between the two atoms is fixed. A triatomic molecule will have six degrees of freedom, three of translation and three of rotation[2]. A pair of compasses has got seven degrees of freedom while two rigid arms connected by a universal joint has nine.

The number of degrees of freedom of a system is additive in the sense that the number of degrees of freedom of a complex system consisting of several individual constituents is equal to the sum of the number of degrees of freedom of these constituents because a knowledge of the configuration of the entire system is just equivalent to a knowledge of the configurations of the constituents. Thus a gas consisting of N monatomic molecules is a dynamical system having $3N$ degrees of freedom; if the molecules be diatomic the degrees of freedom are $5N$, provided the atoms are assumed not to oscillate along their joining line.

When we take elastic bodies, we have further to consider the vibrations due to the elastic displacement of its component particles. X-ray investigations show that the atoms in the solid can be regarded as independent entities and may thus be regarded as its component particles. The simplest kind of vibration is given by a simple harmonic motion and the energy in this case is represented by two squared terms, *viz.*, $\frac{1}{2}m\dot{x}^2+\mu x^2$, where x is the displacement. The first term represents the kinetic energy and the second represents the potential energy. Now we know in the case of a S. H. M. that the mean kinetic energy is equal to the mean potential energy. Hence the average energy corresponding to one vibration is equal to twice the kinetic energy corresponding to one degree of freedom. We may say that the vibration of an atom in an elastic solid along one coordinate is equivalent to two degrees of freedom.[1] Thus if the elastic solid consists of N atoms, the total number of degrees of freedom will be $N\times 3\times 2$, for each atom is free to vibrate along the three coordinate axes.

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[1] This may also be defined as the number of independent squared terms occurring in the expression for the energy of the system.

[2] In general if a molecule consists of n atoms, quite free to move, it will have $3n$ degrees of freedom. Thus if $n=2$, $F=6$. The sixth degree of freedom which was neglected above is the vibration of the atoms along the line of centres. Alternatively we may regard these degrees of freedom to be due to three for each of the atoms. Thus the total number may be counted in different ways.

3·25. Boltzmann's Extension of Maxwell's Law.—Let us now apply these considerations to a vessel containing a polyatomic gas in thermal equilibrium. The total energy E of a molecule is given by $E=E_t+E_r+E_v$ where E_t, E_r, E_v respectively denote the energy of translation, of rotation and of vibration. The molecules of the gas will be colliding with one another and the energy corresponding to any degree of freedom for a molecule at any instant will vary within wide limits, as a matter of fact, between 0 and ∞. We have therefore to extend the scope of the distribution law to include the other possible motions. This was done by Boltzmann. In fact the law is very general and is applicable to liquids and solids as well. The law in this general form can be proved from statistical mechanics. For doing so we must consider the motion of a general dynamical system. Any dynamical system[2] having n degrees of freedom needs n coordinates of position to specify its configuration at any instant. These are generally denoted by $q_1, q_2 \ldots\ldots q_n$, and are called the '*generalised coordinates*' of the system. The generalised components of velocity are $\dot{q}_1, \dot{q}_2 \ldots\ldots \dot{q}_n$. Classical mechanics tell us that if we know these $2n$ coordinates of position and velocity at any instant, the motion of the system for any future time can be determined. It is found more convenient to replace these velocity coordinates by the corresponding *generalised momenta* $p_1, p_2 \ldots . p_n$ defined by the relation $p_n = \partial E/\partial \dot{q}_n$ where E denotes the total energy of the system, and p_n is called the generalised momentum conjugate to q_n. Thus if the system is a moving particle of mass m, the positional coordinates usually chosen are x, y, z and the corresponding momenta are p_x, p_y and p_z being equal to $m\dot{x}$, $m\dot{y}$, $m\dot{z}$ respectively. Similarly if the system is capable of small vibrations, the vibrational motion can also be defined in terms of p's and q's.

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[1] This follows directly from the second way of defining 'degrees of freedom'.

[2] For a rigid body rotating about an axis fixed in itself the degree of freedom is one and the generalised coordinate is simply the angle θ which a fixed direction in the body makes with a fixed direction in a plane perpendicular to the axis of rotation.

The potential energy V of a dynamical system will be a function of the q's only. The kinetic energy L in all ordinary cases will be a homogeneous quadratic function of the velocities $\dot{q}_1$, . . . $\dot{q}_n$ and may therefore be written in the form $L = \Sigma a_{rs} \dot{q}_r \dot{q}_s$. The p's defined by the relation $p_r = \partial L/\partial \dot{q}_r$ are thus linear functions of $\dot{q}$'s and therefore the expression for energy can also be expressed by linear transformation as a homogeneous quadratic expression in the p's. We can thus express L as

$$L = \Sigma b_{rs} p_r p_s \quad . \quad . \quad . \quad . \quad (41)$$

and the total energy

$$E = L + V. \quad . \quad . \quad . \quad . \quad (42)$$

With the aid of generalised dynamical treatment Boltzmann showed that the law of distribution of particles having their motion defined by any set of p and q and contained within the range q, $q+dq$, p, $p+dp$ is given by

$$f(p, q)\, dp\, dq = Ce^{-E(p, q)/kT}\, dp\, dq, \quad . \quad . \quad (43)$$

where $E(p, q)$ is the energy corresponding to the state of the particle denoted by p and q. The proof of this general theorem[1] is given in Chap. IX.

3·26. Law of Equipartition of Kinetic Energy.

—We shall now deduce the law of equipartition of energy* which states that in a dynamical system in thermal equilibrium the energy is equally distributed between the various degrees of freedom and for each of them it is equal to $\frac{1}{2}kT$. The law was first arrived at by Maxwell in 1859 and was later shown by Boltzmann to hold for the energies of rotation and vibration also. More rigorous proofs were given later from statistical mechanics by Lorentz, Gibbs and others. The elements of this deduction will be found in Chap. IX where equation (43) is deduced.

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[1] As experimental verification of this extended form of Maxwell's law we may mention, in addition to what is given in §3·21 — 3·22 the application of this formula to explain the band spectra and specific heat of diatomic molecules (Chap. XVI) and also the deduction of the vapour pressure formula with its help. For the last see Bradford, *Phil. Mag.*, **48**, 936, 1924, and connected papers.

The quadratic expression in the p's given in equation (41) can be transformed into a sum of square of the form

$$L = \tfrac{1}{2}(a_1\xi_1^2 + a_2\xi_2^2 + \ldots.). \quad . \quad . \quad . \quad . \quad (44)$$

where ξ_1, ξ_2 . . . are the new variables called "momentoids," and a_1, a_2 . . . are coefficients which may depend upon the coordinates of position q_1, q_2 . . . . . This follows from the well-known property of quadratic forms of being resolved into a sum of squares. The ξ's are some linear functions of the p's and the distribution law (43), can be expressed in terms of the momentoids in the form

$$f(\xi, q)\, d\xi\, dq = Ae^{-E(\xi, q)/kT}\, d\xi\, dq, \quad . \quad . \quad . \quad (45)$$

where A is a new constant.

From (42) and (44) the total energy $E(\xi, q)$ can be expressed in the form

$$E = \tfrac{1}{2}\alpha_1\xi_1^2 + E',$$

where E' represents the energy corresponding to the other momentoids and coordinates, and $\frac{1}{2}\alpha_1\xi_1^2$ denotes the part of the energy corresponding to the momentoid ξ_1. α_1 is independent of ξ_1 but in general it may be a function of the q's. Hence from (43)

$$dn = nAe^{-(\frac{1}{2}\alpha_1\xi_1^2 + E')/kT}\, d\xi_1 d\xi_2 \ldots . dq, \quad . \quad . \quad . \quad (46)$$

where the constant A is given by the relation

$$\int \ldots \int Ae^{(-\frac{1}{2}\alpha_1\xi_1^2 + E')/kT}\, d\xi_1\, d\xi_2 \ldots . dq = 1, \quad . \quad . \quad (47)$$

or

$$A = \frac{1}{\int e^{-\frac{1}{2}\alpha_1\xi_1^2/kT} d\xi_1 \int \ldots . \int e^{-E'/kT} d\xi_2 \ldots dq}, \quad . \quad (48)$$

for the variables ξ_1, ξ_2, . . . q_1, q_2, ... are all independent, and hence the integral may be regarded as a product of two integrals.

The mean energy corresponding to the momentoid ξ_1 is

$$\frac{1}{n}\int \tfrac{1}{2}a_1\xi_1^2 dn = \int \tfrac{1}{2}a_1\xi_1^2 A e^{-(\frac{1}{2}a_1\xi_1^2+E')/kT}\, d\xi_1 d\xi_2 \,..\, dq,$$

$$= \frac{\int \tfrac{1}{2}a_1\xi_1^2 e^{-\frac{1}{2}a_1\xi_1^2/kT}\, d\xi_1 \int \ldots \int e^{-E'/kT}\, d\xi_2 \ldots dq}{\int e^{-\frac{1}{2}a_1\xi_1^2/kT}\, d\xi_1 \int \ldots \int e^{-E'/kT} d\xi_2 \ldots dq},$$

by substituting the value of A from (48). The limits of integration are $-\infty$ and $+\infty$ for all the variables. Since the second integral in both the numerator and the denominator are identical, they cancel out and the expression for the mean energy becomes[1]

$$\frac{\int_{-\infty}^{+\infty} \tfrac{1}{2}a_1\xi_1^2\, e^{-\frac{1}{2}a_1\xi_1^2/kT} d\xi_1}{\int_{-\infty}^{+\infty} e^{-\frac{1}{2}a_1\xi_1^2/kT}\, d\xi_1} = \tfrac{1}{2}kT. \quad . \quad . \quad (49)$$

Thus the mean kinetic energy for the momentoid ξ_1 is $\frac{1}{2}kT$. Similarly for the other momentoids also. Thus we see that there is equipartition of energy between the different momentoids. It will be seen that this result is essentially due to the assumption that the kinetic energy can be expressed as a sum of squared terms. It is always possible to identify three momentoids with the translational motion of the centre of gravity of a molecule and hence the energy of translational motion for each degree of freedom is $\frac{1}{2}kT$. The momentoid ξ may refer to vibration also. By suitable transformations[2] it can be shown that this result is also applicable to rotational kinetic energy.

3·27. Molecular and Atomic Energy.—The above theorem is very useful in calculating the total molecular energy of substances. We shall now use it to calculate the specific heat of gases. In monatomic gases the molecules are identical with atoms and if, as a first approximation, we assume the atom to be a structureless point, then from the previous considerations each molecule has got three degrees of freedom, and a system containing a gram-molecule of the gas will have altogether $3N$ degrees of freedom, N being the number of molecules in a gram-molecule of the gas. In the state of a perfect gas the molecules will have no potential energy. Therefore the energy of a gram-molecule of a monatomic gas is

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[1] Since a_1 cancels out in the integration with respect to ξ_1 as seen in equation (49) it does not affect the remaining integrals though it may be a function of the q's.

[2] For details see Kennard, *Kinetic Theory of Gases* (1938), pp. 365-366.

$$E = 3N \times \tfrac{1}{2}kT = \tfrac{3}{2}NkT.$$

The molar specific heat at constant volume is therefore

$$C_v = \partial E/\partial T = (3/2)R = 2 \cdot 98 \text{ cal./degree.}$$

For all perfect gases $C_p - C_v = R$, hence

$$C_p = 5R/2 = 4 \cdot 96 \text{ cal./degree,}$$

and the ratio of the two specific heats

$$\gamma = 5/3 = 1 \cdot 66. \quad . \quad . \quad . \quad . \quad . \qquad (50)$$

These theoretical conclusions agree with experimental results (See Table 4, p. 105) for monatomic gases like argon, helium, etc.

The atoms, however, are not structureless points but have finite size and cannot be regarded as solid elastic spheres. It is now established beyond doubt that the atoms are complex systems composed of a positively charged nucleus and shells of electrons. Such a system possesses rotational motion as well as internal vibrations. As a matter of fact, the component electrons by virtue of their vibrations, give rise to spectral lines. But these motions can be excited only at very high temperatures (*Vide* Chap. XVI) and can be entirely neglected for our present purpose. The rotational motion can also be neglected as the electrons have negligible mass, and the whole mass of the atom is concentrated in the nucleus which has an extremely small radius. The moment of inertia is therefore extremely small, of the order of 10^{-40} gm. $\times$ cm.^{2} and hence from the foregoing classical principles the energy of rotation will be extremely small. It can be shown from the quantum theory that the energy required to set up an atom in rotation is rather large, hence we are justified in assuming that at ordinary temperatures such motions do not exist.

In *diatomic* gases the molecules can be pictured as made up of two atoms joined rigidly to one another like a dumb-bell. Treating the atoms as points the molecule will have three degrees of freedom of translation and two of rotation about the two axes perpendicular to the line joining the atoms. Thus the total energy

E of a gram-molecule of a perfect diatomic gas is given by $E = \frac{5}{2}RT$. Hence

$$C_v = \tfrac{5}{2}R;\ C_p = \tfrac{7}{2}R;\ \gamma = 1{\cdot}4. \qquad (51)$$

This is approximately the case for H_2, N_2, etc. (p. 105). If however we take into account the structure of the atom, it is obvious that there will be three degrees of translation, three of rotation and a number of vibrational ones. The third degree of rotation about the joining line will be ineffective so far as C_v is concerned, much in the same way as for monatomic gases. The vibrational motion consists of oscillations of the atomic masses along the line of centres and is treated in Chap. XVI, but the vibrational energy is generally small for the gases at ordinary temperatures. It appears however to be appreciable in the case of chlorine and other halogens even at room temperatures where C_v is found to be greater than $\frac{5}{2}$R. Eucken discovered that in the case of H_2 at low temperatures C_v falls to $\frac{3}{2}$R. This indicates that the rotations disappear in the case of hydrogen at low temperatures. The fall is however very gradual and not in multiples of $\frac{1}{2}$R; hence it cannot be fully explained by simply saying that the rotations disappear. For a full explanation of these difficulties see Chap. XVI.

In a *triatomic* gas a molecule possesses three translational and three rotational degrees of freedom, and hence

$$C_v = 6\times\tfrac{1}{2}R = 3R;\ C_p = 4R;\ \gamma = 1{\cdot}33. \qquad (52)$$

It is not possible to calculate in a simple way the energy of internal vibrations of polyatomic molecules since the vibrations are not freely and fully developed but are considerably restricted and restrained. It is however easy to see that with greater complexity of the molecule, γ will diminish but will always be greater than 1.

An expression for the specific heat of solids may also be obtained from the kinetic theory. Consider a gram-atom of solid containing N atoms. As shown already this system has $6N$ degrees of freedom and therefore its energy is $6N\times\frac{1}{2}kT$. Hence the specific heat of a gram-atom at constant volume is $3R = 5{\cdot}96$. This yields Dulong and Petit's law.

But the kinetic theory of specific heat is unable to explain the variation of specific heat with temperature (§2·25) particularly the marked decrease at extremely low temperatures both in solids and in gases. Further the decrease is gradual and cannot be explained by the disappearance of any degree of freedom which would involve discontinuous changes by multiples of $\frac{1}{2}R$. We cannot assume fractional degrees of freedom. Here then there is a complete failure of classical dynamics and equipartition law. The quantum theory of specific heat (Chap. XVI) has been developed which explains the existing facts satisfactorily.

MEAN FREE PATH PHENOMENA

3·28. Need for the Assumption that Molecules have got a Finite Diameter.—We have seen in the previous sections that the molecules of a gas are moving at ordinary temperatures with very large velocities; in the case of air it amounts to about 400 metres per second. There is no force to restrain the motion of the molecules. Hence during the early days of the kinetic theory, the objection was raised that the assumption of such large rectilinear velocities was incompatible with many facts of observation. If the particles are moving with such enormous velocities, the gaseous mass contained in a vessel would disappear in no time. But we are all aware that the top of a cloud of smoke holds together for hours; hence there must be some factor which prevents the free escape of particles.

A very simple explanation was offered by Clausius. He showed that the difficulty disappears if we ascribe to the molecules a finite though very small volume. Then as a molecule moves forward, it is sure to collide with another molecule after a short interval, and its velocity and direction of motion will be completely changed. In the further development of the kinetic theory therefore we shall assume that the molecules are small in comparison with the average inter-molecular distance but not vanishingly small. As a first approximation we assume that the molecules are small elastic solid bodies free from mutual force-action. The results will also be applicable to small-field molecules, where the mutual force-action is negligible except when the molecules are

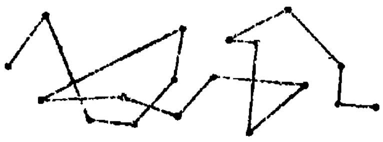

Fig. 16.—Illustration of free path.

very close together, as this is more or less equivalent to the molecules having a slightly bigger size and behaving as an elastic body. Hence for elastic or small-field molecules the free path traversed between two successive collisions will be a straight line described with a constant velocity, since the molecules exert no force over one another except during collision. Thus the path of a single particle will consist of a series of short zig-zag paths as illustrated in Fig. 16.

Some of these free paths will be long, others will be short. We can define a mean free path λ. Add up the lengths of a large number of free paths and divide it by the total number; this will give us the mean free path λ. This quantity is of great importance in studying a class of phenomena, called transport phenomena, which we shall discuss presently.

3·29. Mean Free Path and Collision Probability.—A molecule traversing through the gas suffers collisions quite irregularly in course of time. Considered over a long time, however, there is a certain average rate of collisions per second called the *collision rate* P. The relation between the mean free path and the collision rate can be readily obtained. If the average velocity of a molecule is c, the distance traversed by it in time t is ct. The number of collisions suffered by the molecule in time t is Pt. Hence the average distance traversed between successive collisions, *i.e.*, λ is given by

$$\lambda = \frac{ct}{Pt} = \frac{c}{P}. \qquad (53)$$

Similarly if we confine our attention to those free paths only where the molecule has the velocity c we get

$$\lambda_c = c/P_c \qquad (54)$$

where λ_c and P_c denote the mean free path and the collision rate for molecules of the velocity c only.

The quantity P_c may also be treated as *collision probability* per unit time for a molecule since the number of collisions suffered by a group of n molecules in the time t is $nP_c\,t$ from the previous definition of P_c and the probability or chance that a molecule suffers collision in the time t is $P_c\,t$ or P_c per unit time. Of course we are here assuming that the probability of collision in the time

dt is proportional to the time dt which is a consequence of the assumed molecular chaos.

The number of molecular collisions occurring per second in a gas consisting of n molecules is not nP but only $\frac{1}{2}nP$ since in the former expression we have reckoned each collision between two molecules as two collisions for the two colliding molecules.

3·30. To calculate the Probability of a free Path x.—As mentioned above a molecule describes a free path sometimes longer than the mean free path and sometimes shorter. We shall now calculate the probability that a molecule moving with the velocity c can traverse a path x without suffering collision. This will clearly be a function of x, say $f(x)$. The probability that it will suffer a collision in traversing a further distance dx in time dt is $P_c dt = P_c dx/c = dx/\lambda_c$ from (54). Therefore the probability that the molecule traverses the further distance dx without suffering collision is $1 - dx/\lambda_c$. Hence the probability that it will suffer no collision as it describes the distance $x + dx$ is the product of these two factors since the second probability is independent of the first one. It is therefore equal to

$$f(x).\,(1 - dx/\lambda_c). \quad . \quad . \quad . \quad . \quad (55)$$

Now this must equal $f(x+dx)$, for $f(x+dx)$ is the probability that the path $x+dx$ will be traversed without collision. Therefore

$$f(x+dx) = f(x).(1 - dx/\lambda_c),$$

which from Taylor's theorem yields

$$f'(x)dx = -f(x)\, dx/\lambda_c.$$

Integrating we get

$$\log f(x) = -\frac{x}{\lambda_c} + \text{const.},$$

or

$$f(x) = Ae^{-x/\lambda_c}$$

where A is a constant. To determine A we note that for $x = 0$, $f(x)$ must be equal to unity. Hence $A = 1$ and

$$f(x) = e^{-x/\lambda_c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

This is the law of distribution of free path. From this it is clear that the probability of describing very long paths is extremely small. We thus see that if N_0 molecules of velocity c are incident on the gas, then only the number N_0e^{-x/λ_c} will have travelled the distance x without suffering collision.[1] If however the molecules have velocities distributed according to Maxwell's law we must integrate[2] the above expression for all values of c from 0 to ∞.

3·31. Expressions for Mean Free Path.—With the aid of the above expression we can find the value of the mean free path. First we make the simplifying assumption that all molecules except the one under consideration are at rest. Let this particular molecule B be projected into the gas and let us suppose that the gaseous mass is divided into parallel layers of infinitesimal thickness d, the thickness being so small that it does not contain more than one molecule (Fig. 17). During its path the moving molecule will collide with such other molecules in the layer whose centres lie within a distance σ from the path traced out by the centre of this molecule, σ being the diameter of the molecule[3], or, in other words, it will collide with those whose centres are contained in a circle of radius σ and area $\pi\sigma^2$ described about the centre of the moving particle. $\pi\sigma^2$ is called the mutual collision cross-section of the incident and the stationary molecule. It follows that the probability of the projected molecule not suffering collision with the other molecules in a layer

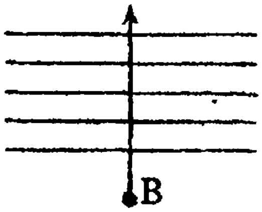

Fig. 17.—A molecule projected into the gas.

$$= 1 - \frac{\text{total collision cross-section of stationary molecules}}{\text{area of the layer}}$$

$$= 1 - \pi\sigma^2 nd,$$

where n is the number of molecules per unit volume.

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[1] It is seen that this law is similar to Biot's law in optics giving the intensity of an incident beam after it has traversed the distance x. The number of incident molecules is decreased, so to say, by reflection and scattering by the other molecules.

[2] For details see Jeans, *Kinetic Theory of Gases* (1940), p. 144.

[3] The sphere of radius σ described about the centre of this molecule is called its sphere of influence for the other molecules.

Hence as the molecule traverses a thickness x, the number of layers passed is x/d and the probability that it does not suffer a collision is

$$(1-\pi\sigma^2 dn)^{x/d}.$$

In the limit $d=0$, hence the probability becomes equal to

$$Lt_{d=0}\left\{(1-\pi\sigma^2 dn)^{(1/n\pi\sigma^2 d)}\right\}^{n\pi\sigma^2 x} = e^{-n\pi\sigma^2 x}.$$

But from the last section this is equal to $e^{-x/\lambda}$, hence we have

$$\lambda = \frac{1}{n\pi\sigma^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (57)$$

Thus the mean free path is inversely proportional to n or mn, *i.e.*, density of the gas, and hence also to the pressure, if the temperature is kept constant.

A very easy way of deducing the same result is as follows:—Consider a molecule traversing the gas with velocity v and suppose other molecules to be at rest. The moving molecule will collide with all such molecules whose centres lie in the region traversed by its collision cross-section or by its sphere of influence. The space thus traversed in a second is a cylinder of base $\pi\sigma^2$ and height v, and hence of volume $\pi\sigma^2 v$. This will enclose $\pi\sigma^2 vn$ centres of molecules and hence the number ν of collisions per second is $\pi\sigma^2 vn$. The length of the mean free path

$$\lambda = \frac{v}{\nu} = \frac{v}{\pi\sigma^2 vn} = \frac{1}{n\pi\sigma^2} \quad . \quad . \quad . \quad . \quad . \quad (58)$$

The above deductions are however not correct, because we assumed the other molecules to be at rest.

A first approximation towards reality was made by Clausius when he improved the above result by assuming that all the molecules move with the same velocity v. He obtained

$$\lambda = \frac{3}{4n\pi\sigma^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

Maxwell further corrected the expression by introducing the law of distribution of molecular velocities which must hold in the steady state and obtained the result[1]

$$\lambda = \frac{1}{\sqrt{2}n\pi\sigma^2}. \quad . \quad . \quad . \quad . \quad . \quad (60)$$

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[1] This is called Maxwell's mean free path to distinguish it from another definition of mean free path introduced by Tait and called Tait's mean free path λ_T ; this is the mean of all distances described by the molecules from a given instant to the next collision. Tait's mean free path is found to be about 4 per cent less than Maxwell's mean free path.

The deduction of these results is given in Note 5.

Maxwell's method can be readily utilised to deduce the mean free path in a mixture of gases. Let us suppose that we have molecules of type $a, b, c \ldots s$, with masses m_a, m_b, m_c, . . . concentrations n_a, n_b, n_c . . ., radii r_a, r_b, r_c . . . and mean free paths λ_a, λ_b, λ_c . . . Then it can be shown by a generalization of Maxwell's method that the mean free path of the molecules a is given by the relation

$$\frac{1}{\pi\lambda_a} = \sum_{x=a}^{x=s} n_x (r_x+r_a)^2 \sqrt{1+m_a/m_x}. \qquad (61)$$

We can easily see from simple considerations that the expression will be of this general form. The mean free path λ_a of the particle is given by

$$\lambda_a = v_a/\textit{number of collisions by } a. \qquad (62)$$

Now a suffers collisions with a, b, c . . . etc. Let ν_{aa}, ν_{ab}, ν_{ac}, . . . denote the number of collisions which a suffers with a, b, c . . . respectively. Then it can be shown that[1]

$$\nu_{ab} = v_a \pi (r_a+r_b)^2 n_b \sqrt{1+m_a/m_b}.$$

Hence by substitution in (62) we get equation (61).

If there are only two gases a and b equation (61) yields

$$\frac{1}{\pi\lambda_a} = n_a(2r_a)^2\sqrt{2} + n_b (r_a+r_b)^2 \sqrt{1+m_a/m_b} \qquad (63)$$

which yields equation (60) when there is only one kind of gas, *i.e.*, $n_b = 0$.

3·32. Experimental Determination of the Mean Free Path.—In Note 6, various methods for finding n the molecular density and σ the molecular diameter are given. Since the mean free path $\lambda = 1/\sqrt{2}n\pi\sigma^2$, it can be easily calculated, if n and σ are known. But this is an indirect method. Till 1920, however, there was no direct experimental method for determining this quantity.

In 1920 Born[2] employed the arrangement shown in Fig. 18 to achieve this end. Q is a quartz tube in which silver is heated at S. The silver evaporates and escapes through the narrow slit R. It then passes through a circular hole in each of the four brass discs

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[1] From this simple consideration we do not get the term $\sqrt{1+m_a/m_b}$. A more detailed analysis will yield this term. For details see Kennard, *Kinetic Theory of Gases* (1938), §64, or Jeans, *Kinetic Theory of Gases* (1940), §109-111.

[2] *Phys. Zeits.*, **21**, 578, 1920.

P_1, P_2, P_3, P_4, the distance between successive discs being 1 cm. Each of these discs carries a glass quadrant G such that the apex of the quadrant lies at the centre of the hole (shown separately at P) and each quadrant is displaced through a right angle relative to the next. Thus each would receive one-fourth of the incident beam. The whole apparatus can be evacuated to any desired pressure by means of a vacuum pump and the resulting pressure can be determined with the help of a MacLeod gauge or a Knudsen manometer (Sec. 3·61).

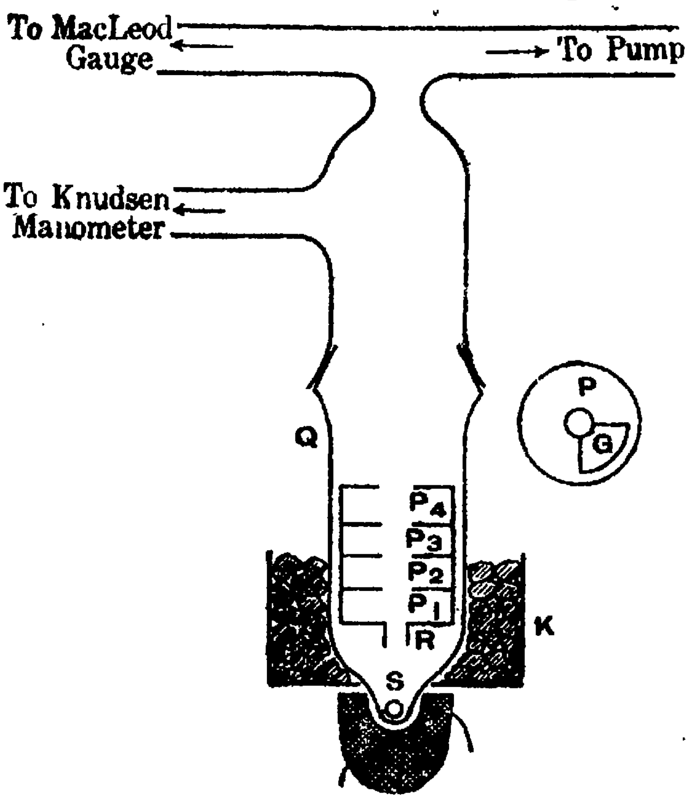

Fig. 18.—Born's apparatus.

The discs are cooled by the cooling mixture K and consequently the silver atoms get deposited on the quadrants. The relative amounts of silver deposited were obtained by a photometric comparison of the density of the deposit. Now if d, d_0 represent the densities of the deposit on the upper and the next lower quadrant respectively, x the distance between them and λ the mean free path, it follows from the law of distribution of free paths that[1]

$$d = d_0 e^{-x/\lambda}. \quad . \quad . \quad . \quad . \quad . \qquad (64)$$

In practice however the beam spreads on the quadrants and the best procedure is to find the density d_{10} on a quadrant when all the gas in the vessel had been pumped out and the free path was equal to the length of the chamber. Next the gas was introduced producing the free path λ and the density d_1 on the same quadrant was found out.

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[1] As shown in §3·30 this result holds accurately for a beam of molecules having identical velocity but here the incident molecules have all possible velocities. Hence equation (64) will hold only approximately in this case.

Then $$d_1 = d_{10}\,e^{-x_1/\lambda},$$

x_1 being the distance of the quadrant from R. Similarly for another quadrant

$$d_2 = d_{20}\,e^{-x_2/\lambda}.$$

Therefore $$\lambda = (x_2-x_1)\log_e \frac{d_2 d_{10}}{d_1 d_{20}}.$$

Now x_2-x_1 was equal to 1 cm. As a result of the experiment it was found that for $p = 5\cdot 8\times 10^{-3}$ mm., $\lambda = 1\cdot 7$ cm. and for $p = 4\cdot 5\times 10^{-3}$ mm., $\lambda = 2\cdot 4$ cm. Hence the product $p\lambda$ is constant as predicted by theory. Thus the mean free path can be experimentally determined and the law of distribution of free paths verified. A little later Bielz[1] repeated the experiment and made considerable improvements in the apparatus. Results similar to the above were obtained.

In these experiments the mean free path λ_{Ag} of silver atoms in a gas was determined. The silver atoms stream from a furnace having the temperature T_{Ag} into a space filled with a gas at T. The concentration of silver atoms in the gaseous space is so small that it can be neglected. It can then be shown that

$$\frac{1}{\pi\lambda_{Ag}} = n(r_{Ag}+r)^2\sqrt{1+\frac{m_{Ag}T}{mT_{Ag}}}, \quad . \quad . \quad . \qquad (65)$$

where m and r are the mass and radius of the molecules comprising the gas, T its temperature; m_{Ag}, r_{Ag} and T_{Ag} the corresponding quantities for silver. The formula is slightly different from (63) because the silver atoms come from a furnace whose temperature is different. For deduction of this modified formula see Born, *loc. cit.* Equation (65) enables us to calculate r_{Ag}, *i.e.*, the radius of the silver atom from experimental data on λ_{Ag}. It was found that $r_{Ag} = 1\cdot 03\times 10^{-8}$ cm. For details of calculation the original paper may be consulted.

3·33. Mean Free Path in a Real Gas.—Uptil now we have assumed that the molecules are rigid elastic spheres free from mutual force-field. In reality, however, they exert forces on one another even at considerable distances and there may be no free paths at all. Encounters at large distances will, however, be so feeble as to produce very small and insignificant deflection. The procedure adopted is therefore to calculate the total deflection produced by assuming a suitable force law for the molecular interaction and assume this deflection to be produced by the same gas but with molecules behaving as rigid elastic spheres of suitable diameter. This diameter is called the *equivalent rigid*

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[1] *Zeits. f. Physik*, **32**, 81, 1925.

sphere diameter and its value depends upon the particular transport property of the gas utilised to give a measure of the collision cross-section or the average deflection from the experimental data. Thus the rigid sphere diameter or the effective mean free path is different when calculated from diffusion and from viscosity and thermal conduction if the molecule does not behave as a rigid sphere as is actually the case.

For very light molecules at low temperatures wave mechanics (Note 15) should be utilised in place of classical mechanics to calculate the deflection produced in a molecular encounter and yields slightly different results. These have been confirmed by the experiments of Knauer[1] on the scattering of hydrogen and helium molecules by mercury vapour. In the case of electrons, when the velocity is not too high to produce ionization or excitation of the molecule, the mean free path λ_e can be calculated from eqn. (63). In several experiments a beam of electrons is allowed to pass through a gas. The concentration of electrons is always very small and its radius and mass can be neglected. Eqn. (63) then yields

$$1/\pi\lambda_e = n_a r_a^2,$$

or

$$\lambda_e = 4\sqrt{2}\,\lambda_a = 5\cdot 6\,\lambda_a \quad . \quad . \quad . \quad . \quad (66)$$

The experiments of Lenard, Mayer,[2] Ramsauer[3], Brode[4] and others confirmed this result when the velocity of the electrons is not too low. For electrons of abnormally low velocity Ramsauer found that the collision cross-section becomes abnormally large. This is known as Ramsauer effect and has been successfully explained from wave mechanics.

Problems.—1. A shower of 1000 molecules, each originally moving with the same velocity, traverses a gas. Calculate the numbers which will be travelling undeflected even after traversing distances equal to 0·2, 0·5, 1, and 2 times the mean free path.

2. Prove that in a gas at ordinary pressures the number of molecules striking unit area of the wall per second is $\frac{1}{4}n\bar{c}$.

The number of molecules per c.c. having the velocity lying between c and $c+dc$ is say $n_c\,dc$. The number of collisions suffered by these in 1 sec. is $\frac{1}{2}P_c\,n_c\,dc$ where P_c is the collision probability. Thus the number of molecules per c.c. coming straight from collision in 1 sec. is $P_c\,n_c\,dc = (c/\lambda_c)\,n_c\,dc$. Consider the molecules striking the area dA of the surface in a direction making an angle θ with the normal to the surface and contained within the solid angle $d\omega$. Those coming from a distance lying between l and $l+dl$ in the above specified direction were contained in an element of volume $l^2\,d\omega\,dl$. Thus the total number of molecules in that volume element is $(c/\lambda_c)\,n_c\,dc\,l^2\,d\omega\,dl$ and of these the fraction $(dA\,\cos\theta)/4\pi l^2$ move in the desired direction. Of this group of molecules only the fraction e^{-l/λ_c} can reach the surface dA. Hence the number of molecules striking the area dA in 1 sec. is, since $d\omega=2\pi\sin\theta\,d\theta$,

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[1] *Zeits. f. Physik*, **80**, 80, 1933; **90**, 559, 1934.

[2] *Ann. d. Physik*, **64**, 451, 1921. [3] *Ibid*, **64**, 513, 1921.

[4] *Phys. Rev.*, **25**, 636, 1925.

$$dA\int_0^\infty n_c\,dc\times c\int_0^{\pi/2}\frac{1}{4\pi}2\pi\sin\theta\cos\theta\,d\theta\int_0^\infty\frac{1}{\lambda_c}\,e^{-l/\lambda_c}\,dl=\tfrac{1}{4}n\bar{c}\,dA.$$

3. Use the idea of free path to calculate the pressure exerted by a perfect gas.

From the last expression the normal momentum imparted by molecules striking the area dA in 1 sec. is

$$dA\int_0^\infty n_c\,c\,dc\int_0^{\pi/2}\tfrac{1}{2}\sin\theta\cos\theta\,d\theta\times mc\cos\theta\int_0^\infty\frac{1}{\lambda_c}\,e^{-l/\lambda_c}\,dl$$

$$=m\,dA\int_0^\infty n_c\,c^2dc.\,\tfrac{1}{6}=\tfrac{1}{6}\,nm\overline{c^2}\,dA.$$

Taking into account the equal contribution of reflected molecules also, the pressure $p=\frac{1}{3}\,mn\overline{c^2}$.

TRANSPORT PHENOMENA

3·34. Non-Equilibrium Gases and their Properties.—We have so far considered gases in equilibrium and have shown in §3·18 that for a gas in equilibrium Maxwell's law of distribution of velocities is satisfied, *viz.*,

$$dn=n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}e^{-\frac{m}{2}\frac{(u^2+v^2+w^2)}{kT}}\,du\,dv\,dw.$$

The expression will be modified if the gas is endowed with mass motion, i.e., the entire gas or a portion of it is moving as a whole. Let the components of the mass velocity at any place be u_0, v_0, w_0. Then the actual velocity of a molecule represented by u, v, w, in space is made up of two parts :—(1) The mass velocity represented by u_0, v_0, w_0; (2) the random thermal velocity represented by $u-u_0$, $v-v_0$, $w-w_0$. It is easy to see that corresponding to the thermal motion u, v, w in the former case without mass motion, the analogous quantities now are $u-u_0=U$, $v-v_0=V$, $w-w_0=W$. Hence the distribution law becomes[1]

$$dn = n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}(U^2+V^2+W^2)}\, dU\, dV\, dW. \quad . \quad . \quad (67)$$

This holds rigorously when u_0, v_0, w_0, T, n are constant throughout the gas. We would expect that this law might hold even if these quantities vary from point to point. Unfortunately rigorous analysis shows that this is not quite so and that (67) is only a first approximation. For the present however we shall assume the truth of (67).

If the gas is not in an equilibrium state (it may perhaps be in a steady state) any three of the following cases, singly or jointly, may occur. (1) u_0, v_0, w_0 may not have the same value in all parts of the gas so that there will be a relative motion of the layers of the gas with respect to one another. It is shown below that in such a case the layers moving faster lose momentum to the slower moving layers. This gives rise to the phenomenon of viscosity. (2) T may not be the same throughout, then we have the phenomenon of conduction, *viz.*, thermal energy will pass from regions of higher T to regions of lower T. (3) If n is not the same everywhere we have the case of diffusion, *i.e.*, molecules from regions of higher concentration pass to regions of lower concentration. It is thus obvious that *viscosity, conduction and diffusion represent respectively the transport of momentum, energy and mass.* These are therefore called *transport phenomena* and are irreversible in the thermodynamic sense. We shall not treat these phenomena with mathematical rigour, but shall adopt a treatment which, though only approximate, gives a vivid physical picture of their mechanism. More rigorous treatment has been given by Maxwell, Boltzmann, Meyer, Jeans, Chapman, Enskog, and others[2].

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[1] Since u_0, v_0, w_0 are very small in comparison to u, v, w (u_0 being a few cms./sec. while u is about 10^4 cm./sec.), the streaming velocity is of little influence in modifying Maxwell's distribution law.

[2] For full details of the rigorous calculation *The Mathematical Theory of Non-Uniform Gases* by Chapman and Cowling (C. U. Press, 1952) may be consulted. For simpler exposition see Jeans, *Kinetic Theory of Gases* (1940), Chap. IX.

These phenomena are brought about by the thermal agitation of the molecules. The molecules carry with them certain associated magnitudes corresponding to the layer from which they come and thereby tend to neutralise the differences in u_0, v_0, w_0, T and n. But the molecules move with very large velocities, while these processes are comparatively very slow. The cause of this anomaly lies in the frequent molecular collisions. Hence the study of these phenomena is most conveniently done through the mechanism of free path. A molecule describing a free path λ is in effect transporting its momentum, energy and mass through a distance λ. In case of gases in equilibrium this is balanced by an equal transfer in the opposite direction ; in other cases there is a continuous transfer of these magnitudes giving rise to the transport phenomena.

3·35. Viscosity.—Maxwell in 1860 was the first to explain this on the kinetic theory. Since then rigorous proofs have been developed but we shall give here an elementary treatment based on consideration of mean free path. Consider a gas, uniform in temperature and density, moving parallel to the horizontal xy plane. Thus there is a mass motion of the gas parallel to the xy plane but no mass motion along the z-axis. Assume that the mass velocity u_0 in the direction of the x-axis increases upwards as z increases.

The molecules above the plane $z=z_0$ possess, on the average, greater x-momentum than those below it, and hence when molecules from either side cross the dividing plane there is greater transport of momentum downwards, since the number of molecules moving each way is the same, there being no mass motion parallel to the z-axis. Thus any particular layer gains in x-momentum and thereby experiences an accelerating viscous force parallel to its direction of motion. We shall first give a rough calculation of this viscous force.

In order to simplify the calculation we may suppose that every molecule traverses a distance λ equal to the mean free path and then suffers a collision. The molecules however will be coming from all directions with all possible inclination to the z-axis. We may therefore roughly take the average projection of λ on the z-axis as[1] $\frac{1}{2}\lambda$. Thus the molecules crossing the plane z_0 may be assumed to have suffered their last collision at a distance $\frac{1}{2}\lambda$ above or below the plane and will therefore be bringing the momentum appropriate to that plane. It is easily seen that for any layer $\bar{u} = u_0$ where $\bar{u}$ denotes the component velocity averaged over all molecules in the layer. If the velocity gradient is du_0/dz the difference in the mean molecular velocity across two planes separated by a distance $\frac{1}{2}\lambda$ is $\frac{1}{2}\lambda\, du_0/dz$, since λ is small compared with the scale of variation in u_0. The mass of a molecule being m, the excess of momentum transferred by it downwards is given by $\frac{1}{2}m\lambda du_0/dz$. Again due to random motion, the number of molecules crossing unit area of a layer per second downwards will be of the order of $n\bar{v}$ or more precisely (see §3·33, problem 2) $\frac{1}{4}n\bar{v}$, where n is the molecular density and c the mean molecular velocity of the gas. Hence the positive momentum transferred across the plane downwards is $\frac{1}{8}mn\bar{c}\lambda\, du_0/dz$ and an equal amount of negative momentum is transferred upwards. Thus the net transfer of positive momentum downwards is $\frac{1}{4}mn\bar{c}\lambda du_0/dz$. This will exert an accelerating force on the lower layer, or the lower layer will retard this faster layer by a force equal to this. From the definition of viscosity this force must equal $\eta\, du_0/dz$. Hence[1]

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[1] More accurately this will be $\frac{2}{3}\lambda$.

$$\eta = \tfrac{1}{4}mn\,\bar{c}\,\lambda = \tfrac{1}{4}\bar{c}\,\rho\lambda, \qquad . \quad . \quad . \quad . \quad (68)$$

where ρ is the density of the gas.

This result has been obtained from various crude assumptions. We shall now examine the phenomena in greater detail.

3·36. Detailed Analysis.—In the foregoing it was assumed that all the gas molecules traversed the mean free path λ and brought the same average momentum. Now we shall consider the molecules moving at random in all directions and find from considerations of probability the number moving in any direction with a certain free path. Further a law of distribution of velocities will be assumed which may not be Maxwellian as the gas is not in equilibrium state.

Let the velocity gradient exist along the z-axis as before. Suppose a molecule after suffering collision at P (Fig. 19) travels with velocity components u, v, w and crosses the plane $z = z_0$ at Q.

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[1] Had we substituted the correct value $\frac{2}{3}\lambda$ instead of $\frac{1}{2}\lambda$ we would have got as the correct value $\eta = \frac{1}{3}\bar{c}\rho\lambda$.

The gaseous layer as a whole moves on account of its mass velocity u_0, say from R to Q, in the time that the molecule moves from P to Q. The molecular velocity c of the molecule thus has the components $u-u_0$, v, w relative to the layer. Let $\mu = mu$ denote the momentum of a molecule and $\bar{\mu}$ the average value of the momentum for any layer. Thus $\bar{\mu}$ increases with z and is a function of z only. Denote $\bar{\mu}$ for the z plane by $\bar{\mu}\,(z)$.

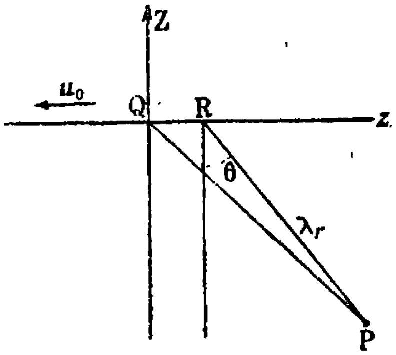

Fig. 9

Let us denote PR, the path traversed by the molecule relative to the gaseous layer, by λ_r and denote the angle it makes with the z-axis by θ. Hence the value of $\bar{\mu}$ for the plane of P is

$$\bar{\mu}(z_0 - \lambda_r \cos\theta) = \bar{\mu}(z_0) - \lambda_r \cos\theta \frac{d\bar{\mu}}{dz},$$

since $z = z_0 - \lambda_r \cos\theta$ for this plane. We can assume[1] that the molecules after suffering collision in a small element of volume at P will, on the average, have a velocity equal to the mass velocity of the layer at P and that all the past history of the molecule is immaterial. These molecules, therefore, on the average, carry the momentum pertaining to the layer at P, *viz.*,

$$\bar{\mu}(z_0) - \lambda_r \cos\theta \frac{d\bar{\mu}}{dz}. \quad . \quad . \quad . \quad . \quad . \quad (69)$$

The number of molecules coming from unit volume near P in the direction lying between θ and $\theta+d\theta$ is

$$\frac{n}{4\pi}.\ 2\pi \sin\theta\, d\theta = \frac{n}{2} \sin\theta\, d\theta,$$

where n represents the molecular density, $2\pi \sin\theta\, d\theta$ the solid angle corresponding to the direction lying between θ and $\theta+d\theta$.

Of these only a fraction $f(c)\,dc$ have velocities lying between c and $c+dc$ where

$$\int_0^\infty f(c)\,dc = 1.$$

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[1] According to Jeans this assumption is not valid on account of the persistence of velocities discovered by him.

Now the molecules of the above description which cross unit area of the plane $z = z_0$ near R per second are only those which are contained in a cylinder of base unity in the plane z_0 and of height $c \cos \theta$. Hence the total number of molecules having velocity between c and $c+dc$ and crossing the plane per unit area per second is

$$\tfrac{1}{2}n \sin \theta \, d\theta . \, f(c) \, dc . \, c \cos \theta .$$

The momentum carried by these molecules is

$$\frac{nc}{2} f(c) \, dc . \, \sin \theta \cos \theta \, d\theta \left\{ \bar{\mu}(z_0) - \lambda_c \cos \theta \frac{d\bar{\mu}}{dz} \right\} . \qquad (70)$$

Instead of λ_r we have put $\lambda_c = \bar{\lambda}_r$ because these molecules may have suffered their last collision in any layer and hence we must use the mean value of λ_r for molecules of the velocity c moving towards the fixed plane z_0. This is equal to λ_c the mean free path for molecules moving with velocity c and not $\frac{1}{2}\lambda_c$ as one might think, because when the molecule has left Q its probability of collision is just the same[1] whether the molecules suffered the last collision at Q or at P. Hence the mean distance traversed beyond the plane z_0 before subsequent collision is λ_c and similarly the mean distance to the plane is also λ_c. Therefore the total momentum carried by the molecules per second is

$$\int_0^\infty c f(c) \, dc . \, \frac{n}{2} \int_0^\pi \sin \theta \cos \theta . \left\{ \bar{\mu}(z_0) - \lambda_c \cos \theta \frac{d\bar{\mu}}{dz} \right\} d\theta$$

$$= \int_0^\infty c f(c) \, dc \left[-\frac{n}{3} \lambda_o \frac{d\bar{\mu}}{dz} \right] = -\tfrac{1}{3} (\Sigma c \lambda_c) \frac{d\bar{\mu}}{dz} ,$$

where $\Sigma c \lambda_c$ denotes the summation of the product of the molecular velocity and the mean free path for all molecules. If we put $\Sigma c \lambda_c = n\bar{c}\lambda$ where λ denotes the mean free path defined in another way and $\bar{c}$ the mean molecular velocity, the above expression becomes

$$-\tfrac{1}{3} n \bar{c} \lambda \frac{d\bar{\mu}}{dz} . \qquad (71)$$

Hence there is a downward transport of momentum equal to

$$\tfrac{1}{3} mn\bar{c}\lambda \frac{du_0}{dz} .$$

since $\bar{\mu} = m\bar{u} = mu_0$.

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[1] For detailed discussion of this point see Kennard, *Kinetic Theory of Gases* (1938), p. 141.

As mentioned above this is equal to the viscous drag $\eta\, du_0/dz$ exerted by the faster moving upper layer. Equating these two expressions we have

$$\eta \frac{du_0}{dz} = \tfrac{1}{3}\, mn\bar{c}\lambda \frac{du_0}{dz},$$

or

$$\eta = \tfrac{1}{3}\, mn\bar{c}\lambda = \tfrac{1}{3}\rho\bar{c}\lambda, \quad . \quad . \quad . \quad (68a)$$

where ρ is the density of the gas.

Expression (68*a*) requires correction for the various approximations we have introduced into the calculations. Firstly we have not defined what this new mean free path means. Detailed calculations, by using the value of λ_c and assuming the distribution $f(c)$ to be Maxwellian, show that this mean free path is 1·051 times Maxwell's mean free path for elastic spheres. Further we have disregarded the velocity distribution in writing (69) and the free path distribution in writing expression (70). A more serious error however lies in the assumption that the velocity distribution $f(c)$ is Maxwellian. Calculations show that molecules which come from regions of higher mass velocity retain after collision some of this excess velocity and therefore there is a greater transport of momentum than that given by (71). Jeans calculates the effect of this persistence of velocities and finds in consequence that expression (71) should be multiplied by 1·38 approximately. No final equation has been given by this method embodying all necessary corrections.

The exact numerical coefficient has been found by Chapman[1] and by Enskog[2] from rigorous mathematical methods. It is easily realised that the viscous force is really due to the departure of the gas from Maxwell's distribution law caused by the laminar motion of the gas. The momentum transferred across any z-plane will be given by $\Sigma\, mu.\, w$, where w is the component velocity perpendicular to the plane. The problem is thus to discover the distribution law in a shearing gas. The solution was obtained by Chapman and by Enskog on two different lines. They obtained the value 0·499 in place of $\frac{1}{3}$ in equation (68*a*) for rigid elastic spheres. For details *vide* Jeans, *Dynamical Theory of Gases*, Chapters VIII and IX.

3·37. Discussion of the Result.—We have established that $\eta = \frac{1}{3}\rho\bar{c}\lambda$, but $\lambda = 1/\sqrt{2}n\pi\sigma^2$ from (60). Hence

$$\eta = \frac{1}{3\sqrt{2}}\,\frac{m\bar{c}}{\pi\sigma^2}. \quad . \quad . \quad . \quad . \quad (72)$$

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[1] *Phil. Trans.*, **211**, 433, 1912; **216**, 279, 1915; **217**, 115, 1916; *Proc. Roy. Soc.*, **93**, 19, 1916.

[2] "Kinetische Theorie der Vorgänge in mässig verdünnten Gasen", Dissertation, Upsala, 1917.

Now $\bar{c}$ is proportional to the square root of the absolute temperature, hence the coefficient of viscosity is independent of the pressure or the density of the gas and depends only upon the temperature. This result was first predicted by Maxwell from theoretical considerations. Though it appeared somewhat improbable, it was subsequently confirmed[1] experimentally by Meyer,[2] Maxwell[3] and others who showed that this holds true for pressures from a few mm. of mercury upto several atmospheres. This confirmation constitutes one of the most striking triumphs of the kinetic theory. Maxwell took a system of three coaxial discs fixed to a common axis and suspended it by a torsion thread inside a vessel containing air. These discs were placed between four fixed discs placed very close to them and were made to execute torsional oscillations. Maxwell found that the oscillations die at the same rate whether the air was dense or rare showing that the viscosity is independent of density.

At very low pressures however this law fails. This is because as we lower the pressure, the mean free path λ gradually increases till it becomes comparable with the dimensions of the vessel, and after that it can increase no further on account of the arrangement of the apparatus and becomes constant. Any further decrease of pressure reduces ρ and hence η from (68), because λ remains constant. We may also look at the phenomena in a different way. Under these conditions molecular collisions become rare and the basis of our previous calculation fails. Now the effects of the individual molecules must be simply additive and therefore viscosity will be proportional to the density. Thus at very low pressures the coefficient of viscosity should rapidly decrease with decrease of pressure. This conclusion was verified by Crookes[4] who observed the oscillations of a vertically suspended leaf of mica in gases upto a pressure of a few thousandth mm.

At very high pressures also, Maxwell's law is found to fail as revealed by the experiments of Warburg and von Babo[5] who determined the viscosity of CO_2 from 60 atmospheres to 107 atmospheres and found that the viscosity of CO_2 increases much faster as the density is increased.

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[1] For a discussion of this experimental evidence see Meyer, *Kinetic Theory of Gases*, pp. 181-188.

[2] *Pogg. Ann.*, **125**, 40, 564, 1865; **143**, 14, 1871.

[3] *Phil. Trans.*, **156**, 249, 1866.

[4] *Phil. Trans.*, **172**, 387, 1881.

[5] *Wied. Ann.*, **17**, **390**, 1882.

This departure from Maxwell's law at high pressures is due to the fact that at these high pressures the mean free path is becoming comparable with molecular diameters and the transport is not through λ but through $\lambda + \sigma \cos \theta$. Enskog has shown that the effect of this is to cause η/ρ to vary according to the relation

$$\frac{\eta}{\rho} = \frac{1}{2 \cdot 545}\left[\frac{v}{b} + 0 \cdot 8 + 0 \cdot 7614\frac{b}{v}\right]\left(\frac{\eta}{\rho}\right)_{\text{min.}},$$

where b is the van der Waals' constant and v the volume of the gas. Thus η/ρ passes through a minimum for $v = 0 \cdot 8726b$. This relation has been fairly well verified by Michels and Gibson[1] for nitrogen in the range 15 to 965 atmospheres.

Again since $\bar{c}$ varies as $1/\sqrt{m}$, η for different gases should vary as $\sqrt{m}$. Actually however σ also varies from gas to gas to some extent, and if we take this variation of σ into account, this result is found to hold pretty well.

3·38. Variation of Viscosity with Temperature.—Since $\bar{c}$ varies as $\sqrt{T}$, the coefficient of viscosity should vary as $\sqrt{T}$ but actually it is found to vary much more rapidly. The reason for this discrepancy is the assumption made in the foregoing theoretical treatment that the molecules are rigid elastic spheres devoid of mutually interacting forces. In reality however the molecules are surrounded by fields of force whose magnitude is difficult to determine. Assuming these forces to be repulsive, it is evident that with the increase in temperature and the consequent increase in molecular velocities, the molecules will penetrate into each other's field of force at collision to a greater degree. This means that the effective size of the molecules decreases at higher temperatures producing an increase in viscosity from eqn. (72). Assuming the repulsive force between two molecules separated by the distance r to be μr^{-s} it can be shown that $\eta \propto T^n$ where[2]

$$n = \tfrac{1}{2} + \frac{2}{s-1}.$$

$s = \infty$ for elastic spheres when $n = \frac{1}{2}$ in agreement with (72); molecules with large s are called 'hard' and those with small s 'soft'. Thus with this assumption of the inverse power law the viscosity can be written in the form

$$\eta = AT^n, \quad . \quad . \quad . \quad . \quad (73a)$$

where A is a constant for the substance. This formula is fairly well obeyed by helium, hydrogen and a number of other gases, but fails in several cases.

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[1] *Proc. Roy. Soc.*, **134**, 307, 1931.

[2] This relation between n and s was inferred by Rayleigh from dimensional considerations.

Sutherland proceeded on the assumption that the molecules are rigid spheres with a weak attractive force between them which falls off rapidly with distance. The effect of the attractive forces is to increase the number of collisions. This is equivalent to a decrease in λ or increase in σ, the effective diameter of the molecule. Detailed calculation shows that the results can be correctly expressed if for σ^2 we substitute

$$\sigma_\infty^2\left(1+\frac{b}{T}\right),$$

where σ_∞ is the value of σ at $T=\infty$, σ is the molecular diameter at $T°$, and b some constant. Hence the variation of η with temperature will be given by

$$\eta=\frac{A\sqrt{T},}{1+b/T}, \quad . \quad . \quad . \quad . \quad . \quad (73b)$$

where A is a constant. This law was found by Schmidt[1] to hold for air, hydrogen, helium, argon, etc., between -195 and 185°C, but Onnes[2] and others found it inadequate for hydrogen and helium at very low temperatures.

Attempts were made by Lennard-Jones[3], Hasse and Cook[4], Buckingham[5], Buckingham and Corner[6] to improve upon the law of force. Lennard-Jones assumed the law

$$f(r)=\frac{A}{r^n}-\frac{B}{r^m}, \quad . \quad . \quad . \quad . \quad . \quad (74a)$$

with $n>m$. Usually from considerations of dispersion energy (§10·14) the attractive force exponent m is put equal to 7. The Lennard-Jones (12, 6) potential

$$\phi(r)=4\epsilon\,[(\sigma/r)^{12}-(\sigma/r)^6], \quad . \quad . \quad . \quad . \quad (74b)$$

where ϵ is the maximum energy of attraction and σ is the collision diameter for low-velocity head-on collisions, has been found very successful in explaining the transport properties of gases and the necessary numerical computations have been done by Hirschfelder, Bird and Spotz[7], and by Kihara and Kotani[1]. A quantum-mechanical treatment of the problem has been given by Uehling and Uhlenbeck[2], Massey and Mohr[3] and others. For detailed discussion see Kennard, *loc. cit.* pp. 150—160, or Chapman and Cowling, *loc. cit.* Chap. XII, or Hirschfelder, Curtiss and Bird, *loc. cit.*

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[1] *Ann. d. Physik*, **30**, 393, 1909.

[2] *Proc. Amst. Akad.*, **15**, 1386, 1913.

[3] *Proc. Roy. Soc.*, **106**, 463, 1924; *Proc. Phys. Soc. London*, **43**, 461, 1931; *Physica*, **4**, 941, 1937.

[4] *Proc. Roy. Soc.*, **125**, 196, 1929.

[5] *Proc. Roy. Soc.*, **168**, 264, 1938.

[6] *Ibid*, **189**, 118, 1947.

[7] *J. Chem. Phys.*, **16**, 968, 1948.

3·39. Conduction.—Let us now investigate the similar problem of the conductivity of a gas. In this case the temperature and hence the energy varies from layer to layer and it is the energy E which is transferred from one layer to another. Proceeding exactly as in §3·36 and replacing μ by E, the total transfer of energy per unit area is given by

$$-\tfrac{1}{3}n\bar{c}\,\lambda\,\frac{d\bar{E}}{dz}. \quad . \quad . \quad . \quad . \quad . \qquad (75)$$

If K be the conductivity of the gas, dT/dz the temperature gradient, the flow of energy across unit area will be $-JK\,dT/dz$, where J is the mechanical equivalent of heat. Therefore

$$JK\frac{dT}{dz}=\tfrac{1}{3}n\bar{c}\,\lambda\,\frac{d\bar{E}}{dT}\,\frac{dT}{dz},$$

or

$$K=\tfrac{1}{3}\,n\bar{c}\,\lambda\,\frac{d\bar{E}}{dT}\,\frac{1}{J}=\tfrac{1}{3}n\bar{c}\,\lambda.mc_v=\eta c_v, \quad . \quad . \qquad (76)$$

when c_v the specific heat is expressed in heat units, for $d\bar{E}=Jmc_v dT$.

The above relation is however found to be at variance with experimental results. The derivation given above is not rigorous for reasons explained in §3·36. Many attempts have been made to make improvements in this approximate method, for example those by O. Meyer and Jeans[4], but these have not met with much success. Chapman[5] and Enskog, following Maxwell's method, discussed rigorously the transport of energy by spherically symmetrical (monatomic) molecules and showed that energy is transported at 5/2 times[6] the rate given by the expression (75). This result is found to be in accordance with experiments.

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[1] *Proc. Phys. Math. Soc. Japan*, **25**, 602, 1943.

[2] *Phys. Rev.*, **43**, 552, 1933.

[3] *Proc. Roy. Soc.*, **141**, 434, 1933; **144**, 188, 1934.

[4] Jeans, *Dynamical Theory of Gases*, 4th edition, pp. 291-299.

[5] *Phil. Trans.* A, **211**, 433, 1912 and other papers.

[6] This holds when we assume the molecules to repel each other with a force varying as r^{-s} where r is the distance between the centres of the molecules and s is put equal to 5. For values of s between 5 and ∞, $K/\eta c_v$ lies between 2·50 and 2·522.

For the general case of any molecule we may put

$$K/\eta c_v = \epsilon. \qquad (77)$$

It is difficult to determine ϵ for polyatomic molecules since their energy is partly due to translational motion and partly to internal motions. The investigations of Enskog or Chapman give only the transport of translational energy. It might well be that the translational energy is transported faster than the internal energy because we know that the fastest moving molecules carry the largest amount of translational energy. The ratio of internal energy to translational energy in the transported molecule has not yet been calculated by rigorous methods. Eucken[1] has suggested that in the case of polyatomic gases the transport of other forms of energy may be given by (76) while that of the translational energy is given by Chapman's results. With this assumption he found an expression for ϵ. Let the total number of degrees of freedom of the molecule be $3+\beta$ where β denotes the number due to causes other than translation. Then the expression for the transport of energy becomes

$$\frac{\eta}{m}\left[\frac{5}{2}\frac{d\bar{E}_t}{dT}+\frac{d\bar{E}'}{dT}\right]\frac{dT}{dz}. \qquad (78)$$

where $\bar{E}_t$ is the translational energy and $\bar{E}'$ the energy of other types. As before this is equal to $JK\frac{dT}{dz}$. Equating these two expressions we have

$$\frac{K}{\eta}=\frac{1}{Jm}\left[\frac{5}{2}\frac{d\bar{E}_t}{dT}+\frac{d\bar{E}'}{dT}\right].$$

From the law of equipartition we have

$$\frac{d\bar{E}_t}{dT}=\frac{3}{2}k;\ \frac{d\bar{E}'}{dT}=\frac{\beta}{2}k.$$

Hence we get

$$\frac{K}{\eta}=\left[\frac{5}{2}\cdot\frac{3}{2}+\frac{\beta}{2}\right]\frac{k}{Jm}. \qquad (79)$$

We can express this result in terms of c_v and γ. From the law of equipartition

$$c_v=\frac{3+\beta}{2}\frac{R}{JM};\quad c_p=\frac{5+\beta}{2}\cdot\frac{R}{JM},$$

whence

$$\gamma=1+\frac{2}{3+\beta};\ c_v=\frac{k}{Jm(\gamma-1)}. \qquad (80)$$

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[1] *Phys. Zeits.*, **14**, 324, 1913.

Equation (79) after substitution for β and k/Jm from (80) yields

$$\frac{K}{\eta c_v} = \epsilon = \tfrac{1}{4}(9\gamma - 5). \qquad \qquad (81)$$

Hence for *monatomic* gases, $\epsilon = 2\cdot5$, for *diatomic* gases, $\epsilon = 1\cdot9$, etc.

The agreement of experimentally determined values with theoretical results is shown in table[1] 2 and is surprisingly good in view of the crudeness of our assumptions.[2]

Table 2.—Values of K and $K/\eta c_v$.

Gas	K (obs.) $\times 10^6$ in cal. cm.$^{-1}$ sec.$^{-1}$°C.$^{-1}$	$\eta \times 10^6$ in gm. cm.$^{-1}$ sec.$^{-1}$	c_v in cal. per gm. per °C.	$K/\eta c_v$ (obs.)	$\frac{1}{4}(9\gamma - 5)$.
Helium	352	188·7	0·745	2·51	2·50
Argon	39·7	210·4	0·0747	2·53	2·50
Neon	108·7	298·1	0·1477	2·47	2·50
Hydrogen	416	85·0	2·42	2·02	1·92
Nitrogen	58	167·4	0·176	1·97	1·91
Oxygen	58·5	192·6	0·1575	1·91	1·89
CO	55·9	166·5	0·176	1·91	1·91
NO	55·5	179·4	0·167	1·86	1·90
CO_2	35·2	138·0	0·153	1·67	1·68
N_2O	36·8	136·2	0·155	1·74	1·68
Ethylene	40·7	96·1	0·293	1·44	1·56

Since $K = \epsilon\eta c_v$ and the variation of c_v is small, the variation of conductivity with pressure and temperature follows in general the same course as the variation of viscosity. Thus conductivity like viscosity is independent of pressure. This was verified experimentally by Stefan[3] and others. This law however fails at very high and at very low pressures as in the case of viscosity. At extremely low pressures, the conductivity decreases. The mechanism of transport then becomes quite different for which Knudsen[4] has given a theory. As in the case of viscosity, the conductivity of all gases increases more rapidly than the square root of the absolute temperature.

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[1] Compiled from Chapman and Cowling, *Mathematical Theory of Non-Uniform Gases* (1939), p. 241 where full references are given.

[2] This derivation is open to criticism as it assumes that the transport of translational energy is not affected by the presence of internal energy. For a full criticism of this derivation see Chapman and Cowling, *loc. cit.* pp. 238-240.

[3] *Sitzb. Akad. Wiss. Wien*, **65**, 2, 45, 1872.

[4] *Ann. d. Physik*, **32**, 809, 1910 and other papers.

The most reliable experimental data on the thermal conductivity of inert gases obtained by Kannuluik and Carman[1] give a temperature variation which can be satisfactorily accounted for by the Lennard-Jones (12, 6) potential.

3·40. Diffusion.—We may begin by defining the coefficient of diffusion. Take any gas and imagine a horizontal plane drawn in it, and suppose the molecular concentration varies in the vertical direction but is constant along the horizontal plane. Call this vertical direction the z-axis. If we denote the molecular concentration by n, experiments show that for any substance, liquid or gas, the number of molecules ν crossing unit area of the horizontal plane in unit time in the positive direction of the z-axis is

$$\nu = -D\frac{dn}{dz}, \quad . \quad . \quad . \quad . \quad (82)$$

where D is a constant, called the coefficient of diffusion.[2] D obviously depends upon the molecular velocity and hence upon the temperature.

We shall now explain the phenomenon of diffusion also by the mechanism of free path and give a simple theory of diffusion. Assume for the sake of definiteness that two gases, hydrogen and carbon dioxide, are placed one above the other, hydrogen being above. On account of their molecular motion the two gases will mix with each other even against gravity. This diffusion process continues as long as there are inequalities of composition and tends to diminish it continuously. After infinite time the composition will be the same everywhere. Let us denote the concentrations of the two gases in a horizontal plane at any instant by n_1 and n_2. These concentrations will vary in a direction perpendicular to the horizontal plane which we call the z-axis. Thus n_1 and n_2 are functions of z only in this case of one-dimensional diffusion.

Since the pressure and temperature are constant throughout the gas in the usual experiments on diffusion, it follows from Avogadro's law for perfect gases that for all layers

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[1] *Proc. Phys. Soc. London*, **65**B, 701, 1952.

[2] Similarly the number crossing unit area at a distance $z+dz$ is $-D\left(\frac{dn}{dz}+\frac{d^2n}{dz^2}dz\right)$. Hence the excess, *viz.*, $D\frac{d^2n}{dz^2}dz$ remains lodged in the element of volume $dz\times 1$. Hence the rate of increase in the number of molecules per unit volume $d\nu/dt = D\,d^2n/dz^2$. This is the well-known equation of one-dimensional diffusion and is analogous to the equation for thermal conductivity.

$$n_1+n_2 = n = \text{constant.}$$

Therefore $$-\frac{dn_1}{dz} = \frac{dn_2}{dz} = a,$$

Hence $$n_1 = A_1-az, \quad n_2 = A_2+az,$$

where A_1, A_2 and a refer to the plane z_0 across which the molecular transfers are considered.

Let $\bar{c}_1$ and λ_1 denote respectively the mean molecular velocity and the mean free path for molecules of the first type in the gas while $\bar{c}_2$, λ_2 denote the corresponding quantities for the second type. The number of molecules crossing the plane z_0 may be calculated in the same way as for viscosity. The molecules will have suffered their last collision in the plane $z = z_0-\lambda_1 \cos\theta$ and must be having the concentration appropriate to the plane, *viz.*,

$$A_1-a\,(z_0-\lambda_1 \cos\theta).$$

Hence the number v_1 of molecules of the first type crossing unit area in unit time, as in the case of viscosity, is given by

$$v_1 = \int_0^\infty \int_0^\pi \left[A_1-a\left(z_0-\lambda_c \cos\theta\right)\right] \tfrac{1}{2}\sin\theta\cos\theta\, d\theta.\, cf(c)\, dc$$

$$= \tfrac{1}{3}a\lambda_1\bar{c}_1 \text{ in the upward direction.} \qquad (83)$$

Similarly for the second gas

$$v_2 = -\tfrac{1}{3}a\lambda_2\bar{c}_2 \text{ in the upward direction.}$$

Since in general $v_1+v_2 \neq 0$ there would be a tendency for a net transfer of molecules v_1+v_2 in number in the upward direction. This would tend to set up differences of pressure in the gas which however cannot exist as the pressure must remain constant throughout. Therefore the gas continuously adjusts itself against this tendency by a slow mass motion with a mass-velocity w parallel to the z-axis. Evidently this velocity w will be such that there is no net transfer of volume[1] in either direction and will be a function of z. Thus the number of molecules of type (1) actually[2] transferred in the upward direction becomes $\Gamma_1 = v_1 + wn_1$, and of molecules of type (2), in upward direction $\Gamma_2 = v_2 + wn_2$. The condition $\Gamma_1 + \Gamma_2 = 0$ gives $w = -(v_1 + v_2)/(n_1+n_2)$ and hence the true transfer for the case of pure[1] diffusion is

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[1] For perfect gases this would imply from Avogadro's law the equality of transfer of molecules.

[2] More rigorously, we should assume this mass-velocity in the very beginning and use the correspondingly modified Maxwellian distribution law, and in the end use the condition that the transfer is equal in both directions. This is done in the Maxwell-Chapman-Enskog theory.

$$\Gamma_1 = v_1 - \frac{v_1+v_2}{n_1+n_2} n_1 = \frac{v_1 n_2 - v_2 n_1}{n_1+n_2} = -\frac{dn_1}{dz} \cdot \frac{\lambda_1 \bar{c}_1 n_2 + \lambda_2 \bar{c}_2 n_1}{3\,(n_1+n_2)} .$$

But from definition the diffusion current density $\Gamma_1 = -D_{12}\dfrac{dn_1}{dz}$.

$$\therefore D_{12} = \frac{1}{3}\,\frac{\lambda_1 \bar{c}_1 n_2 + \lambda_2 \bar{c}_2 n_1}{(n_1 + n_2)} . \qquad (84)$$

This is generally known as Meyer's formula for the coefficient of diffusion of one gas into another and is symmetrical for the two gases, *i.e.*, $D_{12} = D_{21}$. This is due to the peculiar way of defining pure diffusion.

If the molecules of the two gases are approximately of equal size and mass, we may take λ and $\bar{c}$ to be the same for both. Equation (84) then reduces to[2]

$$D_{11} = \tfrac{1}{3}\lambda_1 \bar{c}_1 = \frac{\eta}{\rho} . \qquad (85)$$

D_{11} may be called the coefficient of self-diffusion of a single gas and is found to be equal to the viscosity divided by the density of the gas. In the above simplified deduction, we have neglected several factors, *viz.*, the dependence of free path upon velocity, the persistence of velocities, etc., correction for which was applied by Jeans and others. Further we assumed the molecules to behave like perfectly elastic spheres. The general theory was given by Chapman[3] and by Enskog who assumed the molecules to repel each other with a force $\propto r^{-s}$. The different analyses only give in place of 1/3 a different constant in equation (85). The analyses of Chapman and Enskog yield for the coefficient of self-diffusion $D = \epsilon\eta/\rho$ where $\epsilon = 1{\cdot}200$ for elastic spheres and $\epsilon = 1{\cdot}543$ for $s = 5$ (Maxwellian molecules). For detailed discussion see Jeans, *Dynamical Theory of Gases*, Chap. XIII (4th Edition).

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[1] Pure diffusion is arbitrarily defined to be one in which the excessive transfer of one constituent is balanced out by a mass-velocity of the gas as explained above.

[2] This can be obtained much more easily. In this case $v_1 = -v_2$ and $w = 0$. The net transfer is $v_1 = \frac{1}{3} a \lambda_1 \bar{c}_1 = -\frac{1}{3}\lambda_1 \bar{c}_1 dn_1/dz$, which must equal $-D\, dn_1/dz$. Therefore $D = \frac{1}{3}\lambda_1 \bar{c}_1$.

[3] *Phil. Trans.*, **217**, 166, 1917.

3·41.—Comparison with Experiments.—We shall now see how far the above investigations are supported by experimental evidence. From equations (84) and (85) we can easily deduce the dependence of D on the temperature and pressure. For $\lambda \propto 1/n \propto T/p$ and $\bar{c} \propto \sqrt{T}$, hence $D \propto p^{-1}\,T^{3/2}$. The experimental measurements on diffusion are not so accurate as in the case of viscosity and thermal conduction but the observed results lead to the conclusion that D varies inversely as p but the power of T lies between 1·75 and 2. The more rapid increase with temperature is obviously due to the attractive forces between the molecules as already mentioned.

We may try to seek an experimental test of the value of ϵ. It is however not possible to measure self-diffusion directly as molecules of the same gas cannot be distinguished from one another but Lord Kelvin has given a method of calculating it from the observed coefficients of diffusion for various pairs of gases. It is however possible to investigate the diffusion of one radioactive isotope into a stable isotope, of para into ortho-hydrogen or of one gas into another of equal molecular mass and similar molecular structure such as the pairs N_2—CO, N_2O—CO_2. Boardman and Wild[1] worked in this way with different pairs but their results were not fully consistent. It is however found from the various experiments that ϵ lies between the above-mentioned limits.

It is however more interesting to investigate the variation of D_{12} with the composition of the mixture, *i.e.*, upon n_1/n_2. Formula (84) predicts a large variation of the diffusion coefficient with relative concentrations of the two gases but experiments show that it is almost independent of the composition. Thus the simple free-path theory fails badly in this case. The discrepancy is considerably minimised when the above expression is corrected for the persistence of velocities as pointed out by Jeans. Stefan first showed that each kind of gas is hindered only by the other gas in its diffusing motion. The exact formulae have been calculated by the methods of Chapman and Enskog. For rigid elastic spheres Enskog gives the approximate relation

$$\frac{D_{12},\, n_1 = 0}{D_{12},\, n_2 = 0} = \frac{1 + m_2^2 / (13m_2^2 + 16m_1m_2 + 30m_1^2)}{1 + m_1^2 / (13m_1^2 + 16m_1m_2 + 30m_2^2)}\,, \qquad (86)$$

while Meyer's formula gives the value m_2/m_1 for this ratio. A series of experiments by Dorn and his students were performed at Halle in Germany to test this dependence of D_{12} upon n_1/n_2 and the results are given in Table[2] 3 (p. 180).

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[1] *Proc. Roy. Soc.*, **162**, 511, 1937.

[2] *Ann. d. Physik*, **29**, 664, 1929; see also Chapman, *Phil. Trans.*, **211**, 478, 1912.

The variation of the diffusion coefficient with composition given by Chapman's formula (last column) is of the same order as the experimental value. The results calculated from Chapman's formula are seen to agree fairly well with the observed values.

Table 3.—*Dependence of* D_{12} *on composition.*

Pair of gases, gas 1 being written first	$\frac{n_1}{n_2}$	D_{12} (observed) in cm.^{2}/sec.	D_{12} (calculated) (Chapman) in cm.^{2}/sec.
H_2—CO_2	3	0·594	0·589
	1	0·605	0·617
	$\frac{1}{3}$	0·633	0·628
He—A	2·65	0·678	0·689
	2·26	0·693	0·694
	1·66	0·696	0·697
	1	0·706	0·706
	0·477	0·712	0·714
	0·311	0·731	0·719

3·42. Thermal and Pressure Diffusion.—We have so far considered the concentration gradient alone to be the cause of diffusion. Diffusion may however be caused by a pressure gradient dp/dz or by a temperature gradient dT/dz. The former is called 'pressure-diffusion' but is difficult to investigate experimentally. The latter is called 'thermal diffusion' and is of great physical importance since this phenomenon depends for its bare existence upon the law of force between the molecules, and therefore a study of this phenomenon throws considerable light on the nature of molecular force-fields. The existence of thermal diffusion was first discovered in liquids experimentally by Ludwig and fully investigated by Soret in 1879-81; hence for liquids it is called the 'Soret effect'. Thermal diffusion in gases was, however, first predicted theoretically by Enskog[1] and by Chapman[2] and was experimentally confirmed later by Chapman and Dootson[3]. A comprehensive account of the experimental work on the subject will be found in the excellent monograph 'Thermal diffusion in gases' by K. E. Grew and T. L. Ibbs (Cambridge Univ. Press, 1952).

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[1] *Phys. Zeits.*, **12**, 533, 1911. [2] *Phil. Trans.*, **217**, 115, 1918.
[3] *Phil. Mag.*, **33**, 268, 1917.

In the usual experiments two bulbs connected by a tube containing a stop-cock were filled with a uniform mixture of the two gases and were then maintained at different constant temperatures for several hours. Then the stop-cock was closed and the gas in each bulb was analysed. Chapman and Dootson worked with a mixture of H_2 and CO_2 in approximately equal proportions, the bulbs being maintained at 230° and 10°C respectively. The ultimate composition of the hot bulb was found to be 44·9 per cent H_2, 55·1 per cent CO_2 and of the cold bulb 41·3 per cent H_2, 58·7 per cent CO_2. Later experiments by Ibbs and his coworkers, Grew, Nier, Waldman and others have confirmed the existence of the effect in other gaseous mixtures as well.

Briefly, the experimental results show that when a temperature gradient is established in a uniform mixture of two gases, the larger and *heavier* molecules move towards the *colder* side and the smaller and lighter ones in the reverse direction, producing thereby inequality of composition in the mixture. This inequality sets up ordinary (concentration) diffusion which acts in the opposite direction tending to annul this inequality of composition. Ultimately a steady state is reached when the opposing influences of thermal and ordinary diffusion balance and in this final state a steady gradient of concentration is set up by the temperature gradient. These considerations further show that the reverse effect may also be expected, viz., when a concentration gradient is established there will be a net transfer of energy producing a temperature gradient. This is called *diffusion thermo-effect* or Dufour effect.

The rigorous theory of thermal diffusion was given by Chapman and Enskog in the years 1911-1917 and is very complicated because in the steady state both concentration gradient and temperature gradient exist. Several attempts have been made to give a simple theory of thermal diffusion, that by Fürth[1] being fairly satisfactory for elementary treatment. In view of the great importance of thermal diffusion Fürth's treatment is given in Note 18 together with a more detailed account of thermal diffusion and its application to the separation of isotopes by the thermal diffusion column.

BROWNIAN MOVEMENT

3·43. Reality of Molecular Motions[2].—We have so far developed the kinetic theory upon the assumption of molecular structure of matter and of the existence of molecular motions, assumptions which cannot be directly verified since the molecules cannot be seen by the naked eye. As already pointed out in §3·11 we get some evidence of the incessant motion of molecules when we observe under a high power microscope or under an ultra-microscope particles suspended in a colloidal solution (Brownian Movement). The characteristics of the phenomena have been fully described in §3·11. We shall now develop a physical theory of its mechanism.

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[1] *Proc. Roy. Soc. London*, **179**, 461, 1942.

[2] A good account of the Brownian movement will be found in J. Perrin, *Atoms* (Constable & Co., London, 1923).

Our studies in physical chemistry show that dilute solutions containing small quantities of dissolved matter exert upon a surface immersed in the solution a pressure, called the osmotic pressure, which can be measured experimentally. This pressure is attributed to the minute invisible molecules of the solute which are dispersed throughout the solvent. Van't Hoff showed that the osmotic pressure is numerically equal to the pressure which the dissolved substance would exert if it were assumed to behave like a gas having the volume and temperature of the solution. From the view-point of the kinetic theory such a concept appears to be quite justified since the suspended particles would be acted on by forces from all sides due to the surrounding molecules of the liquid which will approximately balance, and hence the suspended particle will be sufficiently free to execute its motion like the molecules of a gas. In fact we can treat the dissolved particles as a gas and apply all the gas laws to them. The laws hold for light as well as heavy particles. It appears reasonable to assume that even visible particles, such as the Brownian particles, will obey these laws. As a matter of fact we shall see in the following sections, that almost all the gas laws are applicable to the Brownian particles.

3·44. Vertical Distribution of Particles in an Emulsion under the Action of Gravity.—The Brownian particles form a gas which is in equilibrium under the action of the external force-field due to earth's gravitation. The distribution of pressure will therefore be similar to those prevailing in the case of gases of the earth's atmosphere. We can easily calculate the law of distribution in an isothermal vertical column of the gas composed of Brownian particles.

Consider a layer of the gas bounded by the surfaces at heights z and $z+dz$ on which the pressures are p and $p+dp$ respectively, and suppose z increases upwards. Consider the equilibrium of unit area of the layer. If the density of the gas at z is ρ, the force due to gravity acting on the layer is $g\rho\, dz$. The net force on the layer is $p+dp-p+g\rho dz$ which should be zero for equilibrium. Hence

$$dp = -g\rho\, dz.$$

For a perfect gas $p = nkT$, $\rho = mn$. Hence

$$\frac{dn}{n} = -\frac{mg}{kT}dz = -\frac{Nm}{RT}g\, dz, \quad . \quad . \quad . \quad (87)$$

where N is the Avagadro number. Integrating we obtain[1]

$$n = n_0\, e^{-\frac{Nmg}{RT}(z-z_0)} \quad . \quad . \quad . \quad . \quad . \quad (88)$$

where n and n_0 denote the number of particles per c.c. at the heights z and z_0 respectively. The effective mass m of the suspended particle, since it is buoyed up by the liquid, is equal to $\frac{4}{3}\pi r^3(d-d')$ where r = radius of the granules, assuming them to be spherical, d = density of the granules, d' = density of the inter-granular liquid. Hence

$$N = \frac{3RT}{4\pi r^3(d-d')\,g(z-z_0)}\log\frac{n_0}{n}. \quad . \quad . \quad . \quad (89)$$

This formula furnishes a convenient method of determining the Avogadro number.

Perrin carried out an extensive series of researches in this line. He selected emulsions of gamboge and mastic which were obtained by adding alcoholic solutions of these substances to excess of water. To get particles of uniform size the emulsion was subjected to energetic centrifuging, when the granules deposited as a sediment. The sediment was brought into suspension again and fractional centrifuging was employed to separate grains approximately the same size. Emulsions containing such homogeneous grains are called uniform emulsions. For them Perrin first verified the relation (88), *i.e.*, the exponential variation of n with height, which proves that the theoretical considerations underlying its deduction are fundamentally correct.

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[1] This equation can be written straight from equation (43) expressing Maxwell's equation in the general form, since the potential energy of the particle at the two places is mgz and mgz_0 respectively. Incidentally it shows that a Maxwellian gas will be in hydrostatic equilibrium.

To determine the Avogadro number by means of equation (89) we must determine the density d and the radius r of the granules. Perrin determined the density in three different ways. The simplest way to do this is to find the masses m, m' of water and emulsion respectively, required to fill a specific gravity bottle; then by desiccation in an oven the mass m'' of resin contained in the emulsion is found. If d_0 be the density of water, the volume of the bottle is m/d_0, that of the water contained in the emulsion is $(m'-m'')/d_0$ and hence that of the granules is $\frac{m}{d_0}-\frac{m'-m''}{d_0}$. The mass of the granules being m'' their density is readily calculated.

To find the radius of the granules Perrin again employed three methods. The most convenient however is that involving the use of Stokes' law[1]. Stokes showed that the force required to maintain the motion of a sphere of radius r in a fluid of viscosity η is $6\pi\eta r v$ where v is the velocity of the sphere. If the sphere falls under its own weight the effective force due to gravity is $\frac{4}{3}\pi r^3(d-d')g$. Hence it will move with a final steady velocity v such that

$$6\pi r\eta v = \tfrac{4}{3}\pi r^3(d-d')g,$$

or

$$r^2 = \frac{9}{2}\cdot\frac{\eta v}{(d-d')g}.$$

Thus if we observe the steady velocity of fall of the particles under gravity we can determine the radius r. For this purpose the emulsion is contained in a capillary tube and the rate of fall of the cloud of granules observed.

To measure n of formula (89) a drop of the emulsion is put in a cell formed from a hollow slide about 0·1 mm. in height (Fig. 20). The cell is kept at a constant temperature by surrounding it with a water bath, and a vertical microscope with a high power objective is focussed upon the emulsion. The objective has a small depth of field so that only those grains contained in a thin layer a few microns in thickness can be distinctly seen at a time. Raising or lowering

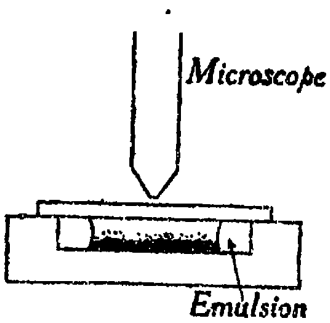

Fig. 20.—Observing Brownian movement.

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[1] For the conditions under which Stokes' law holds true, see Millikan, *The Electron*, and for the deduction of Stokes' law from hydrodynamical principles, see Lamb, *Hydrodynamics*, Chap. XI, sec. 338.

the microscope focusses it upon different layers. As the number of particles in any layer is generally too large to be counted, the field of view is limited by an opaque diaphragm pierced with a central hole. The granules must be suitably illuminated with a strong source of light. As the moving molecules are difficult to count, it is found convenient to take instantaneous photographs and then count the number at leisure. When the distribution in the different layers becomes steady the observations in a certain layer are taken.

The number of particles in a layer is calculated as the mean of several observations at regular intervals. Thus Perrin found for a particular layer $n = 2, 2, 0, 3, 2, 2, 5, 3, 1, 2, \ldots$ giving a mean of 22/10 for the layer. In this way the ratio n_0/n is determined. The vertical displacement of the microscope is read giving $z - z_0$. Formula (89) then gives N. From a series of experiments Perrin deduced the value of N to be $68 \cdot 2 \times 10^{22}$ which is somewhat higher than the value at present accepted.

3·45. Theory of the Translational Brownian Movement.—Starting from the hypothesis that the Brownian movement at right angles to gravity is entirely irregular, Einstein[1] and Smoluchowski[2] independently gave a complete analysis of the phenomenon. We shall first give the simplified treatment due to Langevin.[3] Every particle of the suspension is bombarded from all sides by the molecules of the liquid. The number of these collisions is so large—there will be about 10^{21} collisions per second suffered by a Brownian particle in a liquid under normal conditions and each collision is expected to produce a kink in the path of the particle—that we cannot really speak of separate collisions and cannot hope to follow with our sense of perception the path of a particle in such fine detail. We may therefore assume[4] that the effect of these collisions is to produce an average systematic force representing the dynamical friction or viscous force experienced by the particle and a fluctuating part X of the force which is responsible for the Brownian motion. The viscous force is assumed to be given by Stokes' law. Assuming the particles to be spherical, the viscous force f along any arbitrarily chosen axis x is thus given by

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[1] *Ann. d. Physik*, **17**, 549, 1905; **19**, 371, 1906.

[2] *Bull. intern. acad. Sci. Cracovie*, p. 577, 1906.

[3] *Comp. Rend.*, **146**, 530, 1908.

[4] This *ad-hoc* assumption enables us to pass from the phenomena of discontinuous events to the case of hydrodynamical viscous force in continuous physics and is justified *a posteriori* by its successful prediction of the results.

$$f = -6\pi\eta r v = -c\,\frac{dx}{dt},$$

where v is the velocity of the particle, r its radius and $c = 6\pi r\eta$. The equation of motion for the particle is thus given by

$$m\,\frac{d^2x}{dt^2} = -\,c\,\frac{dx}{dt} + X, \qquad . \quad . \quad . \qquad (90)$$

X being the instantaneous x-component of the force exerted upon it by the molecules of the liquid over and above the viscous force, the latter representing the average of the actual instantaneous forces. The particle suffers collision every instant with the molecules of the liquid (say one collision in about 10^{-21} seconds) and its motion is thereby changed in direction. Thus X will be quite irregular in value and as often positive as negative.[1] The phenomenon is really of the nature of a 'random walk[2]' and therefore in a sufficiently long time t (long compared with the time between successive collisions, *i.e.*, $\gg 10^{-21}$ seconds) the particle will have suffered an average displacement[3] x. For other particles this displacement will have different values and the sum of these displacements taken for all particles will be zero since the displace-

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[1] In writing the equation in this manner we assume that X is independent of the velocity dx/dt and further the rate of variation of X is extremely rapid as compared to the rate of variation of dx/dt. For a critical discussion of this method see Chandrasekhar, *Rev. Mod. Phys.*, **15**, pp. 20-27 (1943).

[2] The problem of 'random walk' is this :—Suppose a man takes a walk of N steps, each one foot long, either forward or backward at random. Where will he probably be at the end of his walk ? Calculation shows that the probability of his being at a distance of s feet from the starting point is

$$P_s = \frac{N!}{\left(\frac{N}{2}+\frac{s}{2}\right)!\left(\frac{N}{2}-\frac{s}{2}\right)!\,2^N} = \sqrt{\frac{2}{\pi N}}\; e^{-s^2/2N}$$

when N is very large. The most probable displacement is therefore zero and the average displacement is $\sqrt{2N/\pi}$, *i.e.*, proportional to the square root of time since N is proportional to time. The average displacement per step is inversely proportional to $\sqrt{N}$ and is negligible when N is very large.

[3] x will be proportional to $\sqrt{t}$.

ments can have positive and negative signs with equal probability. Hence the displacement in a sufficiently long time averaged over all particles is nearly zero.[1] Let us therefore work with the quantity x^2 since x^2 does not change in sign with change in sign of x. Multiplying the above equation by x and remembering that

$$x\frac{d^2x}{dt^2} = \tfrac{1}{2}\frac{d^2}{dt^2}(x^2) - \left(\frac{dx}{dt}\right)^2;$$

and
$$x\frac{dx}{dt} = \tfrac{1}{2}\frac{d}{dt}(x^2),$$

we get
$$\tfrac{1}{2}m\frac{d^2}{dt^2}x^2 - m\left(\frac{dx^2}{dt}\right) = -\tfrac{1}{2}c\frac{d}{dt}x^2 + Xx.$$

Let us now integrate this expression with respect to time. We obtain

$$\tfrac{1}{2}m\Big[2x\dot{x}\Big]_0^t - m\int_0^t \dot{x}^2 dt = -\tfrac{1}{2}c\Big[x^2\Big]_0^t + \int_0^t Xx\,dt. \quad . \quad (91)$$

The first term is negligible in comparison to the second term since x varies as $\sqrt{t}$ for random motion and $\dot{x}$ varies quite irregularly with time due to collisions with the molecules of the liquid; the second term on the other hand increases as t because $\dot{x}^2$ will have some average value in course of time. The last term containing X will not be negligible as due to the randomness of X and the steady increase of x it will vary faster than $\sqrt{t}$.

Now let us average over a large number of particles. This averaging process tends further to suppress the first term since it will have positive values for some particles and negative for others. The last term containing X now almost disappears since it will be positive for some particles and negative for others. Further since the particles are in thermal equilibrium their mean kinetic energy must be given by the equipartition law. Hence the mean kinetic energy for one degree of freedom, *viz.*, $\tfrac{1}{2}m\dot{x}^2 = \tfrac{1}{2}kT$. Therefore

$$\overline{m\int_0^t \dot{x}^2 dt} = \int_0^t m\overline{\dot{x}^2}dt = kT.\,t,$$

the bar denoting the average over particles. Hence equation (91) yields

$$kTt = \tfrac{1}{2}c\overline{\Delta(x^2)},$$

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[1] Actually it will vary as $\sqrt{t/N}$ where N is the number of particles.

where $\Delta(x^2)$ denotes the change in x^2 in the time t. Assuming the particles to start from the origin we have $\Delta(x^2) = x^2$.

Therefore $$\overline{x^2} = \frac{2kT}{c}\tau = \frac{kT}{3\pi\eta r}\tau,$$

where τ is an interval of time sufficiently large to allow a large number of collisions to have taken place.

If we denote the component of the displacement of the particles along the x-axis by Δx instead of x, we have

$$\overline{(\Delta x)^2} = \frac{kT}{3\pi\eta r}\tau = \frac{RT}{N}\cdot\frac{1}{3\pi\eta r}\tau. \qquad (92)$$

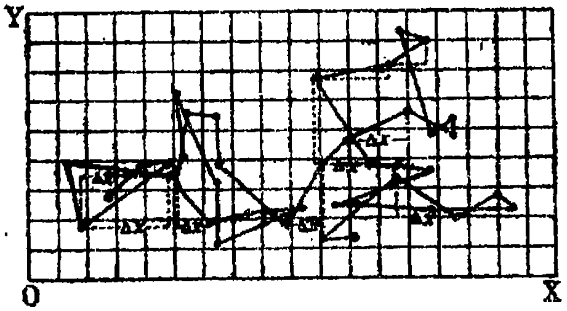

Fig. 21.—Calculating $\overline{(\Delta x)^2}$ from the Brownian motion of a particle.

We shall now see how $\overline{(\Delta x)^2}$ is measured. Instead of observing different particles Perrin watched the motion of a single particle for a long time with the help of a microscope using the camera lucida. The microscope had in its field of view a series of mutually perpendicular lines, as on a graph paper, giving a coordinate system where 16 divisions represented $5{\cdot}0 \times 10^{-3}$ cm. and the position of the particle at intervals of 30 seconds was noted on this coordinate system. From these successive positions the component Δx of the displacement in 30 seconds could be computed as illustrated in Fig. 21 and the mean value of $\overline{(\Delta x)^2}$ for that interval (*viz.* 30 seconds) calculated.

With the help of such measurements Perrin verified equation (92), specially the dependence of $\overline{(\Delta x)^2}$ upon the time τ, the temperature T, the viscosity η, and the radius r. Substituting these values he got the value for N to be $68{\cdot}8 \times 10^{22}$.

3·46. Einstein's Theory of the Translational Brownian Movement.—The foregoing treatment of translational Brownian movement does not throw much light on the physical nature of the phenomenon which however is supplied by Einstein's analysis. It is evident that the Brownian particles, on account of their random motions, tend to diffuse into the medium in course of time; consequently the diffusion coefficient must be related to the Brownian motion[1]. We shall adopt here a very simplified treatment[2] given by Einstein.

Einstein calculates the coefficient of diffusion in two ways :—(1) from the irregular motion of the suspended particles, (2) from the difference in osmotic pressure between different parts due to differences in concentration of the suspended particles which cause the phenomenon of diffusion. Then he equates these two expressions for the diffusion coefficient D.

Let us first calculate D from the random molecular motion. We have seen above that $\overline{(\Delta x)^2}$ is not zero. Let its value for the time τ be Δ^2. Let us assume that the molecular concentration is not uniform but has a gradient along the x-axis causing diffusion of the particles. For simplicity we shall suppose that every particle suffers the displacement Δ in the time τ. Imagine a cylinder with its axis parallel to the x-axis and its end faces S_1 and S_2 separated by a distance Δ. Let the molecular concentrations at these ends be n_1 and n_2 respectively and A denote the cross-sectional area of the cylinder. The number of particles crossing the surface S_1 to the right in time τ is $\frac{1}{2}n_1\Delta A$, for half of the particles contained in the cylinder of volume ΔA situated to the left of S_1 will cross it in time τ. Similarly the number crossing S_2 in the opposite direction is $\frac{1}{2}n_2\Delta A$ and hence the excess crossing a middle layer to the right is $\frac{1}{2}(n_1-n_2)\Delta A$. From the definition of diffusion coefficient this number will be equal to $-D\frac{dn}{dx}\tau A$ where $-dn/dx$ is the gradient of concentration. Hence equating we get

$$\frac{1}{2}(n_1 - n_2)\Delta A = -D\frac{dn}{dx}\tau A.$$

But

$$n_1 - n_2 = -\Delta\frac{dn}{dx}.$$

Hence[3]

$$D = \frac{\Delta^2}{2\tau}. \qquad \qquad (93)$$

We shall now calculate the coefficient of diffusion in the other way. The osmotic pressure acting on the surfaces S_1, S_2 will be p_1, p_2 where, from the gas laws, $p_1 = n_1kT$, $p_2 = n_2kT$. Hence the cylinder experiences a force equal to $(p_1-p_2)A=(n_1-n_2)kTA$ pushing it in the positive direction of the x-axis. This force is thus exerted on the particles contained in the cylinder which are $nA\triangle$ in number, n being the mean concentration. The force acting on a single particle is

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[1] One method of investigating the Brownian motion is therefore to solve the differential equation of diffusion (footnote p. 176).

[2] See *Investigations on the theory of the Brownian Movement* by Einstein, edited by Fürth and Cowper (Methuen & Co.), pp. 68—81.

[3] For a rigorous derivation of (93) see Kennard, *Kinetic Theory of Gases* (1938) p. 286, or *Investigations on the theory of Brownian movement* by Einstein, pp. 12-15.

$$f=\frac{n_1-n_2}{n}.\frac{kT}{\triangle}=-kT.\frac{1}{n}\frac{dn}{dx}.$$

Hence the particle, being suspended in a viscous medium, will move with a steady velocity v given by

$$f=6\pi\eta rv=-kT.\frac{1}{n}\frac{dn}{dx},$$

provided it is assumed to be spherical. Hence

$$nv=-\frac{kT}{6\pi\eta r}.\frac{dn}{dx}.$$

This is equal to the number of particles moving to the right per second per unit area. Since $-dn/dx$ is the gradient of concentration, the diffusion coefficient D will, from definition, be given by

$$D=\frac{RT}{N}.\frac{1}{6\pi\eta r}. \quad . \quad . \quad . \quad . \quad (94)$$

Equating the two values of diffusion coefficient given by (93) and (94) we get

$$\triangle^2=\frac{RT}{N}.\frac{1}{3\pi\eta r}\tau,$$

which is the required equation. Brillouin measured the coefficient of diffusion D and with the help of equation (94) calculated the Avogadro number N. It may be mentioned that equations (93) and (94) have been verified experimentally.

3·47. Translational Brownian Movement in Gases.—The translational Brownian movement in gases can be readily observed if we examine smoke or dust particles with an ultramicroscope. The theory of the phenomenon is exactly the same as given above, only the mean squared displacement $\overline{(\triangle x)^2}$ will be much larger in this case since η for gases is much smaller than for liquids, hence the accuracy of measurements will be much greater. Further we assumed the particles to be spherical and supposed Stokes' law to hold true; the validity of these assumptions is open to question. The experiments with gases were carried out by Millikan and Fletcher[1] in 1911 with oil-drops and these assumptions were dispensed with by working in a way analogous to that used by Millikan in his determination of the electronic charge. The oil-drop carried an electrical charge and was suspended between two suitably charged plates and its Brownian movement in a plane at right angles to gravity was observed. Next the drop was allowed to fall under the field of gravity (mg) and its velocity of fall v_1 noted. Then some charge was given to the plates slightly opposing this motion and the velocity of fall v_2 observed. Hence from Stokes' law

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[1] See R. A. Millikan, *The Electron* (University of Chicago Press).

$$mg = Kv_1, \qquad mg - Xen = Kv_2,$$

where X is the electrical field between the plates in the second case, en the charge carried by the drop and K a constant. Hence

$$\frac{Xen}{mg} = \frac{v_1 - v_2}{v_1},$$

or

$$K = \frac{mg}{v_1} = \frac{Xen}{v_1 - v_2}.$$

As the charge ne on the drop is not known they worked with the same drop carrying different charges and found the highest common divisor for the right-hand side which will correspond to $Xe/(v_1 - v_2)_1$. This is the value of K. Substituting this in the equation for Brownian movement we have

$$\overline{(\Delta x)^2} = \frac{2RT}{N} \cdot \frac{\tau}{Xe/(v_1 - v_2)_1}$$

or

$$Ne = \frac{2RT}{X} \cdot \frac{\tau(v_1 - v_2)_1}{\overline{(\Delta x)^2}}.$$

Millikan and Fletcher found $Ne = 2 \cdot 88 \times 10^{14}$ e.s.u. while the Faraday number from electrolysis is $2 \cdot 89 \times 10^{14}$ e.s.u. This testifies to the accuracy of the theoretical discussions given above and to the accuracy of these experimental investigations. Substituting the value of e this gives $N = 6 \cdot 06 \times 10^{23}$.

3·48. Rotational Brownian Movement.—The Brownian particles also exhibit rotational movement.[1] We can observe the orientation of a particle by finding the angle which a certain plane fixed in the body makes with a plane fixed in space. For the mean square change α^2 in orientation in time τ averaged over all particles, Einstein deduced the formula

$$\alpha^2 = \frac{RT}{N} \cdot \frac{\tau}{4\pi\eta r^3}, \quad . \quad . \quad . \quad . \qquad (95)$$

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[1] Even the highly sensitive galvanometers have been found to execute rotational Brownian movement of the order of 10^{-6} radians (see Ising, *Ann. d. Physik*, **14**, 755, 1932). Kappler (*Ann. d. Physik*, **31**, 377, 1938) observed the Brownian movement with the help of a highly sensitive torsion-balance.

where η is the viscosity of the medium in which the particles are suspended and r the radius of the particle. Perrin verified this expression and used it to deduce the value of N from an actual measurement of α^2. Einstein's deduction is based upon the assumption that the mean kinetic energy of rotation is equal to the mean kinetic energy of a linear vibration and hence these investigations are a direct experimental verification of the equipartition law.

We give below the several independent values for Avogadro number furnished by the phenomena of Brownian movement. Better values have, of course, been obtained by later workers.

Vertical distribution of grains . . .	$68{\cdot}3\times10^{22}$
Translational motion	$68{\cdot}8\times10^{22}$
Rotational motion	65 „
Diffusion	69 „
Brownian movement in gases . . .	60·6 „

LOW PRESSURE PHENOMENA IN GASES

3·49. Effusion.—The phenomenon of effusion or leakage of a gas through fine orifices was first studied by Graham[1] and Bunsen before the rise of the kinetic theory. Graham employed a porous plug having numerous fine interstices. He concluded from his experiments that the velocity of efflux, *i.e.*, the volume of different gases escaping into vacuum per second through such orifices was inversely proportional to the square roots of their specific gravities provided the temperature and pressure of the gases were initially the same. This is known as *Graham's law*. Thus for the same temperature and pressure the rate of leakage of oxygen was found to be approximately one-fourth that of hydrogen and that of chlorine was nearly one-sixth. Graham and Bunsen however worked at mean and high pressures when the mean free path of the gas is small compared to the dimensions of the opening. The effusion under these conditions is governed by hydrodynamical laws, the case being analogous to that of a fluid jet forced out under pressure[2]. At pressures so low that the mean free path is much greater than the dimensions of the opening the phenomenon was studied by Knudsen. He calls this phenomenon

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[1] *Phil. Trans.*, **133**, 573, 1846, Meyer, *Kinetic Theory of Gases*, p. 84.

[2] For fuller discussion see Joos, *Theoretical Physics*, (1946) p. 712.

'*molecular effusion*' as under these conditions the molecules move quite independently of one another, molecular collisions being very rare. An explanation of molecular effusion can be easily given from the kinetic theory.

Let n be the molecular density of the gas and s the area of the hole. Now the number of molecules having velocity lying between c and $c+dc$ and striking the hole in a direction lying within a solid angle $d\omega$ and making angle θ with the normal to the hole in time dt is, as in §3·36,

$$s.\,4n\pi a^3\, e^{-bc^2}\, c^2 dc.\, \frac{d\omega}{4\pi}.\, c\cos\theta\, dt, \qquad . \quad . \quad (96)$$

since the incident molecules have Maxwellian distribution. For the entire beam lying between θ and $\theta+d\theta$, $d\omega=2\pi\sin\theta\, d\theta$. Thus the total number of molecules escaping out of the opening in time dt is

$$s.\,4n\pi\, a^3\int_0^\infty c^3\, e^{-bc^2}\, dc\int_0^{\pi/2}\tfrac{1}{2}\sin\theta\cos\theta\, d\theta.\, dt = s\,dt.\,\tfrac{1}{4}n\bar{c} \qquad . \quad (97)$$

where $\bar{c}$ is the mean molecular velocity (p. 138). Hence the mass of gas escaping out through the opening per second is

$$\frac{s}{4}nm\bar{c}=\frac{s}{4}\rho\bar{c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (98)$$

This gives the mass effusing into vacuum per second. The volume of the gas effusing per second is

$$s\sqrt{\frac{kT}{2\pi m}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (99)$$

i.e., $\propto 1/\sqrt{M}$ or $1/\sqrt{\rho}$, where M is the molecular weight and ρ the specific gravity of the gas.

In case the gas escapes not into vacuum but into a vessel containing the same gas at the same temperature but at lower pressure and density (ρ_2), there will be gaseous flow in the opposite direction equal to $\frac{1}{4}\rho_2 s\bar{c}$, and the net outflow of the gaseous mass per second would be

$$\tfrac{1}{4}\bar{c}\,(\rho_1-\rho_2)s. \quad . \quad . \quad . \quad . \quad . \quad . \quad (100)$$

Now $$\bar{c}=\sqrt{\frac{8RT}{M\pi}}=\sqrt{\frac{8p}{\pi\rho}}=\sqrt{\frac{8}{\pi\rho_0}}, \quad . \quad . \quad . \quad (101)$$

where ρ_0 is the density at a pressure of 1 dyne. Also from Boyle's law $\rho_1=p_1\rho_0$, $\rho_2=p_2\rho_0$. Therefore expression (100) becomes

$$s\sqrt{\frac{\rho_0}{2\pi}}\left(p_1-p_2\right).$$

The volume V_0 of gas escaping out measured at a pressure of 1 dyne is given by

$$V_0 = \frac{s}{\sqrt{2\pi\rho_0}}(p_1 - p_2).$$

In Graham's experiments different gases were allowed to escape through fine holes in a perforated brass plate. In more recent times the effusion of gases through small openings was investigated with great care by Knudsen.

Knudsen[1] investigated the flow of gas through a small hole. One of his holes was made in a platinum sheet of thickness 0·0025 mm. and had a diameter of 0·025 mm. He worked with hydrogen, oxygen and carbon dioxide at pressures ranging from 10 cm. to 0·01 mm. of mercury and found that the above results were verified as long as the mean free path was at least ten times the diameter of the hole. For smaller mean free path the rate of flow was found to be greater than the above value and at sufficiently high pressures such that the mean free path was less than one-tenth of the diameter of the hole, the flow was given by the ordinary hydrodynamical formula. Thus the predictions of the kinetic theory were fully confirmed.

Problems.—**1.** Show that the mean translational energy of molecules that cross a surface in a given time is $2kT$ ergs per molecule.

2. Show that the number of molecules crossing unit area of surface per second in the direction making an angle θ with the normal and contained in the solid angle $d\omega$ is

$$n\bar{c}.\ \frac{d\omega}{4\pi}.\ \cos\theta. \qquad . \quad . \quad . \quad . \quad (102)$$

3·50. Flow of Gases through Tubes.

—The great usefulness of the methods of the kinetic theory is illustrated in their application to the flow of gases through fine tubes. Let us give a general idea of these phenomena. Imagine a closed vessel containing some gas at a certain pressure and communicating with another vessel through a pipe. The second vessel contains the same gas at the same temperature but at a lower pressure. We have now to distinguish between different cases of flow depending on the dimensions of the pipe.

If the pipe be long and narrow and the pressure of the gas be not too low so that the mean free path is small compared to the dimensions of the orifice, the flow of the gas is governed by its viscosity. At these pressures the number of collisions among the molecules is very large and thus viscous forces are brought into play. The mass M^* of gas flowing out per second is given by the well-known hydrodynamical law due to Poisseuille

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[1] *Ann. d. Physik*, **28**, 75, 1909.

$$M^* = \frac{\pi R^4 \rho}{8\eta l}(p_1 - p_2), \quad . \quad . \quad . \quad . \quad (103)$$

where R, l respectively denote the radius and length of the tube, ρ is the mean density of the gas, η its viscosity and p_1, p_2 the pressures at the two ends of the tube. This law can be deduced from classical hydrodynamics and is found to be amply verified by experiments. The coefficient of viscosity η calculated from this formula is found to be independent of pressure over a wide range in accordance with the results of §3·36.

In deducing this law we assume that the velocity of flow varies from a maximum in the centre of the pipe to zero at the walls, *i.e.*, the mass velocity of the gas in contact with the wall is zero. When however we take a capillary tube and reduce the pressure, the law no longer holds. Kundt and Warburg found that the flow under these conditions is much larger than that given by Poisseuille's law, and they pointed out that this phenomenon occurs when the mean free path of the gas is comparable to the diameter of the capillary tube.

The deviation from Poisseuille's law may be explained if we suppose that the gas in contact with the walls is not at rest but slips past them with a velocity v_0, *i.e.*, $v \neq 0$ but equal to v_0 at the walls. It is obvious that if the velocity of the gaseous layer at the wall is v_0, a tangential stress F of the nature of a frictional drag will be exerted by the wall on the gas; F is evidently given by the relation

$$F = 2\pi R l . \, v_0 \epsilon, \quad . \quad . \quad . \quad . \quad (104)$$

where ϵ is a constant called the coefficient of external friction of the gas with the wall. Obviously ϵ must depend upon the nature of the walls and of the gas and upon the nature of the molecular impacts on the walls. In the state of steady motion let us consider the equilibrium of a very thin layer at the wall. The force due to the pressure gradient is negligible since the layer is extremely thin, while the viscous force acting at the lower surface and tending to accelerate the layer is $-2\pi Rl\eta dv/dr$. Equating this to (104) we obtain

$$v_0 = -\frac{\eta}{\epsilon}\cdot\frac{dv}{dr} = -\zeta\frac{dv}{dr}, \quad . \quad . \quad . \quad (105)$$

where ζ is a constant, called the *coefficient of slip*. ζ is of the dimensions of length and represents the distance by which the wall should be displaced backwards if the velocity at the wall is to be assumed zero. Again considering the equilibrium of a cylinder of the gas of radius r we have

$$\pi r^2(p_1 - p_2) = -2\pi rl\eta\frac{dv}{dr}.$$

Integrating this equation with the boundary condition that at $r = R, v = v_0$ given by (105) and proceeding as usual we get[1] instead of Poisseuille's law the expression

$$G = \frac{\pi R^4}{8\eta l}(p_1 - p_2)\rho\left(1 + 4\frac{\zeta}{R}\right). \quad . \quad . \quad . \quad (106)$$

In deducing this expression we have neglected the variation of ρ and ζ with pressure and assumed a constant mean value for them. This expression was fully confirmed by the experiments of Kundt and Warburg. They determined experimentally the value of ζ for different pressures and found that ζ varies inversely as the pressure and is of the order of the molecular mean free path for the gas.

We may interpret the above results also by saying that the behaviour of the gas at low pressures is such as would be obtained under the assumption that the velocity of the upper layers goes on decreasing and reaches zero not at the walls of the tube but at a fictitious wall having a greater radius, *i.e.*, the effective diameter of the tube is increased. Another way of looking at the matter is that the viscosity η of the gas does not remain constant but decreases at these low pressures and hence the flow increases. It may be pointed out that at these low pressures there are very few molecular collisions and it is rather meaningless to talk of the viscosity of the gas.

The deviation from Poisseuille's law was explained by Maxwell in 1879 from the kinetic theory. He developed a theory of this viscous slip which is not quite perfect, but Knudsen has shown from extensive experiments that the ideas of Maxwell are essentially correct. The physical ideas underlying Maxwell's explanation are as follows:—

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[1] For details see Kennard, *Kinetic Theory of Gases* (1938), pp. 293-294.

When a molecule strikes the wall we have to find out the nature of exchanges of velocity in such collisions and the direction in which the molecule will be turned back. Two types of collisions are possible. (*i*) The molecules on colliding with the wall may be specularly reflected, *i.e.*, the velocity component perpendicular to the wall is just changed in sign, while the component parallel to the wall is unaltered. In this case the wall behaves as a perfectly smooth surface and the only pressure exerted on it is normal. The walls would exert no drag and[1] $\zeta = \infty$, *i.e.*, viscosity is not able to have a grip on the wall. (*ii*) In the second type the molecules are reflected diffusely in all directions regardless of their initial direction of incidence. Maxwell assumes that the molecules approaching the surface have a Maxwellian velocity distribution, and those leaving the surface obey the *cosine law* expressed by (102), analogous to the emission of radiation from a surface (Chapter XV), as if they came from a Maxwellian gas at rest near the surface. As suggested by Maxwell the diffuse reflection might be due to the large interspaces between the stationary molecules of the surface of the wall. The gas molecules striking the surface will suffer a number of collisions in these interspaces and will consequently lose their entire momentum and will thereafter suffer diffuse reflection, *i.e.*, reflection will be equally probable in forward as well as backward direction. Another possible mechanism is that the molecules might condense on the surface remaining in contact with it for some time, and thereafter leave the surface in random directions as if they forgot all about their past life and start out on a new existence. The molecules are thus *absorbed and re-evaporated* from the surface in all directions. If the gas is at rest there will be no tangential force exerted on the wall, for the velocity component parallel to the wall both initially and finally is zero. If however the gas be in motion as in the case of flow through tubes, the average velocity component of the layer in contact with the wall before incidence is say v, that after reflection is zero, because the reflection is diffuse. Due to this difference in the tangential velocity of the incident and reflected molecules they will impart a tangential momentum to the walls which will consequently exert a force on the gas. This gives rise to the slip coefficient.

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[1] This follows from equation (105) or (108).

The above are the two extreme cases; in actual practice both types or some intermediate type may occur. For the general case Maxwell assumed that the incident molecules striking the wall impart to it on the average, a fraction f of their tangential momentum; f may be interpreted as the fractional area of the surface reflecting diffusely, the remainder reflecting specularly; it may also be treated as the fraction of the incident molecules which is absorbed and re-evaporated, the remainder $1-f$ being specularly reflected. Maxwell showed[1] that in this case the gas slips past the wall with a velocity v_0 given by

$$v_0 = \frac{\eta}{p}\sqrt{\frac{\pi}{2}\frac{RT}{M}}\left(\frac{2-f}{f}\right)\frac{dv}{dr}, \quad . \quad . \quad . \quad (107)$$

and ζ the coefficient of slip in the Kundt and Warburg expression is given by[2]

$$\zeta = \frac{\eta}{p}\sqrt{\frac{\pi}{2}\frac{RT}{M}}\left(\frac{2-f}{f}\right) = \frac{2}{3}\lambda\frac{2-f}{f}, \quad . \quad . \quad . \quad . \quad (108)$$

where $\eta = \frac{1}{3}\rho\bar{c}\lambda$, $p = \rho RT/M$, $\bar{c} = \sqrt{8RT/M\pi}$. ζ is thus of the order of mean free path λ. Thus we see from (106) that the term which expresses the excess of delivery over that given by Poisseuille's law contains pR in the denominator and can be neglected as long as pR is large. Thus the slip term becomes appreciable only at low pressures, and vanishes at higher pressures.

These ideas were further developed by Knudsen and confirmed by means of ingenious experiments carried out over a wide range of pressures.

3·51. Knudsen's Investigation and Theory of Molecular Streaming.—Knudsen carried out experiments up to very low pressures and found that as the pressure is decreased the flow also decreases, but after a certain stage it begins to increase (see Fig. 24) and finally attains a constant value independent of the pressure. The usual concept of slip is applicable only when the gaseous layer has a thickness many times the mean free path so that at some distance from the boundary the ordinary viscous force comes into existence. Thus Maxwell's theory of slip is unable to explain the bend and the subsequent portion of the curve obtained by Knudsen. The theory is therefore insufficient and was extended by the work of Knudsen. At extremely low pressures the flow becomes constant. It cannot thus depend upon the viscosity of the gas. In fact at this stage intermolecular collisions do not take place and only collisions with the wall are of any importance. The velocity of the gas parallel to the wall is the same all along the cross-section of the tube and the layer in which the slip was formerly observed now extends over the entire cross-section of the tube. In fact the mechanism of flow has become quite different; the process has changed from one of viscous flow to *molecular flow* or *molecular streaming*, as Knudsen calls it. The transition is however not abrupt but gradual as indicated by the bend of the curve in Fig. 24.

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[1] Maxwell, *Scientific Papers*, Vol. **2**, p. 708. For a much simpler proof see Kennard, *Kinetic Theory of Gases* (1938), p. 296.

[2] For specular reflection $f = 0$, and for diffuse reflection $f = 1$. From the experimental values of ζ, Millikan (*Phys. Rev.*, **21**, 217, 1923) has calculated values of f for different gases in contact with various surfaces. For air on glass $f = 0·89$.

Knudsen[1] gave a partial theory of the whole range of phenomena which was subsequently improved by Smoluchowski[2]. The theory explains satisfactorily the constant flow observed at extremely low pressures. The essential idea underlying Knudsen's theory is the assumption that all the molecules striking the wall are *absorbed*[3] and *re-evaporated*[4] from the surface. Knudsen assumes that the direction of the molecule after collision is independent of its direction before collision and further the emitted molecules have a wholly random distribution over all directions. Thus the effect of collision is simply to make the stream of molecules diffuse, and the number of molecules sent by the wall in a direction making an angle θ with its normal is proportional to cos θ [equation (102)]. This is the well-known *cosine law* which Knudsen assumed to hold for this case and his experimental results justify the truth of this assumption at least in the case of glass surfaces with which he dealt. Probably the cosine law holds for all such surfaces whose structure is irregular on account of the presence of adsorbed films but does not hold for such surfaces in which the atoms are regularly arranged as in a crystal lattice.

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[1] *Ann. d. Physik*, **28**, 75, 1909.

[2] *Ann. d. Physik*, **33**, 1559, 1910. This derivation is also given in Kennard, *Kinetic Theory of Gases*, pp. 302-305.

[3] Clausing (*Ann. d. Physik*, **7**, 569, 1930) has been able to calculate the time for which the atoms remain in contact with the wall.

[4] This will happen only at high temperatures. If the temperature of the surface be low the molecules of the vapour are permanently condensed.

Knudsen planned a suitable experiment to obtain a direct proof of the validity of the cosine law. The principle of his arrangement is shown in Fig. 22. The glass sphere A has a hole B which lets in a parallel beam of mercury atoms coming out of a certain aperture O so placed that the line joining the aperture to B strikes the sphere in dS_1. The entire sphere is cooled by liquid air with the exception of the portion dS_1 which is at room temperature, so that molecules on striking the surface dS_1 leave it but get condensed quickly when they subsequently strike other portions of the sphere. It can be shown that if the cosine law is obeyed the number of molecules striking unit area of the sphere has the same value all over the sphere. Knudsen found from his experiments that the mercury layer which was formed on the inner surface of the sphere had the same thickness at all places thereby proving the cosine law.

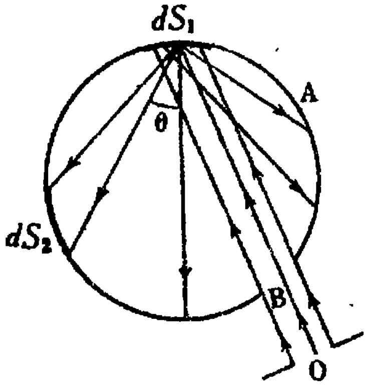

Fig. 22.—Proof of cosine law.

We now proceed to deduce an expression for the molecular flow through a long tube. In the following we adopt Knudsen's method of derivation because it is very simple, though not sufficiently rigorous. A more satisfactory method has been given by Smoluchowski but that is too complicated to be quoted here. Knudsen's method was to equate the momentum imparted to the walls by molecular impacts in a second to the total force acting across the ends of the tube.

Let us calculate the momentum imparted to the walls by the impinging molecules. We will assume that these molecules have a velocity distribution given by Maxwell's law though this will hold only approximately since the gas is in motion and not at rest and is further limited in a space much smaller than the mean free path. Hence the number of molecules of velocity c striking unit area of the wall per second is, as in §3·49

$$4\pi n a^3 e^{-bc^2} c^2\, dc \int_0^{\pi/2} c \cos\theta \,.\, \tfrac{1}{2} \sin\theta\, d\theta = n\pi a^3 e^{-bc^2} c^3\, dc. \quad . \quad (109)$$

These molecules after striking the wall leave it in random directions according to the cosine law and therefore carry no momentum parallel to the wall. Hence the total tangential momentum imparted to the wall is that carried by the incident molecules. Now these molecules are incident on the wall in all directions. Let us denote by w the value of the horizontal component of the velocity c of the molecule averaged over all directions. Evidently $w = k_0 c$, where k_0 is simply an averaging factor and is independent of c. It may be emphasised that in the case of a gas at rest w would be equal to zero but here, on account of the decreasing concentration as we move down the tube, the number of molecules crossing any cross-section towards the region of lower pressure is greater than that crossing in the opposite direction. The result is that on account of this random motion of the molecules a net flow of the gas towards regions of low pressure is produced by the concentration gradient. Evidently then $\sum w = nv$ where the summation extends over all the molecules and v denotes the velocity of flow or streaming. v is assumed to be constant across the cross-section of the tube. Hence

$$k_0 \bar{c} = \frac{\sum k_0 c}{n} = \frac{\sum w}{n} = v. \quad . \quad . \quad . \quad (110)$$

The total momentum imparted to the wall in a direction parallel to it is

$$\int_0^\infty n\pi a^3 e^{-bc^2} c^3 dc \,.\, k_0 c m = \frac{3}{4}\, n k_0 \,.\, kT$$

$$= \frac{3\pi}{32}\, m n k_0 (\bar{c})^2 = \frac{3\pi}{32}\, \rho \bar{c} v, \quad . \quad . \quad . \quad (111)$$

where m is the mass of the molecule and ρ the density of the gas. All this momentum is transferred to 1 cm.² of the wall. Suppose the tube is cylindrical with length l and radius of cross-section r. Then the momentum absorbed by a length dl of the tube by molecular collisions is

$$2\pi r\, dl\, \frac{3\pi}{32}\, \rho v \bar{c}.$$

Equating this to the force across the length dl of the tube which produces it, we have

$$-\frac{dp}{dl}\cdot \pi r^2 dl = 2\pi r\, dl.\frac{3\pi}{32}\rho v\bar{c}.$$

Therefore
$$\rho v = -\frac{dp}{dl}\,\frac{16r}{3\pi\bar{c}}. \qquad . \quad . \quad . \qquad (112)$$

The mass flowing per second

$$M^* = \pi r^2 \rho v = -\frac{16}{3}\,\frac{r^3}{\bar{c}}\,\frac{dp}{dl} \text{ from (112)}$$

$$= \frac{8r^3}{3}\sqrt{\frac{\pi\rho_0}{2}}\,\frac{p_1-p_2}{l}\,, \qquad . \quad . \quad . \quad . \qquad (113)$$

from (101) where p_1, p_2 are the pressures at the two ends and ρ_0 is the density of the gas at a pressure of 1 dyne at the same temperature. The volume flowing out measured at a pressure of 1 dyne is

$$V_0 = \frac{M^*}{\rho_0} = \frac{p_1-p_2}{W_r\sqrt{\rho_0}},$$

where $W_r = \frac{3}{4\sqrt{2\pi}}\cdot\frac{l}{r^3}$ and may be called the 'resistance' of the tube, in analogy with the electrical resistance.

The volume flowing per unit difference of pressure is

$$T_0 = \frac{V_0}{p_1-p_2} = \frac{4}{3}\sqrt{\frac{2\pi}{\rho_0}}\cdot\frac{r^3}{l}\,. \qquad . \quad . \quad . \qquad (114)$$

This equation holds provided the diameter of the tube is small in comparison with the mean free path, and also in comparison with the distance in which an appreciable change in molecular concentration occurs since in deducing (111) we assumed n to remain constant. In case only a fraction f of the molecules are scattered diffusely we must multiply (114) by $(2-f)/f$. We would then obtain[1]

$$T_0 = \frac{4}{3}\sqrt{\frac{2\pi}{\rho_0}}\cdot\frac{r^3}{l}\cdot\frac{2-f}{f}. \qquad . \quad . \quad . \quad . \quad . \qquad (115)$$

3·52. Knudsen's Apparatus.—The original apparatus used by Knudsen[2] is shown in Fig. 23. It consists of two MacLeod gauges

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[1] From the observed flow at low pressures we can calculate f with the help of (115) and then use this value of f to calculate ζ from (108) provided λ is known. We can also compare the values of f obtained in this way from low pressure data with that obtained from high pressure data of the observed slip ζ.

[2] *Ann. d. Physik*, **28**, 75, 1909.

G_1, G_2, which have two bulbs V_1, V_2, sealed to them, for the purpose of holding the gas. U_1 is a graduated U-tube. The capillary through which the flow is to be studied is connected between a_1, and a_2. g_1, g_2, g_3, g_4 are connected by rubber tubings to mercury reservoirs.

By raising or lowering these reservoirs the mercury levels in each of these tubes could be adjusted to any desired position independently of the others. U_2 is connected to the pump while the tube at H is connected to a reservoir of the experimental gas.

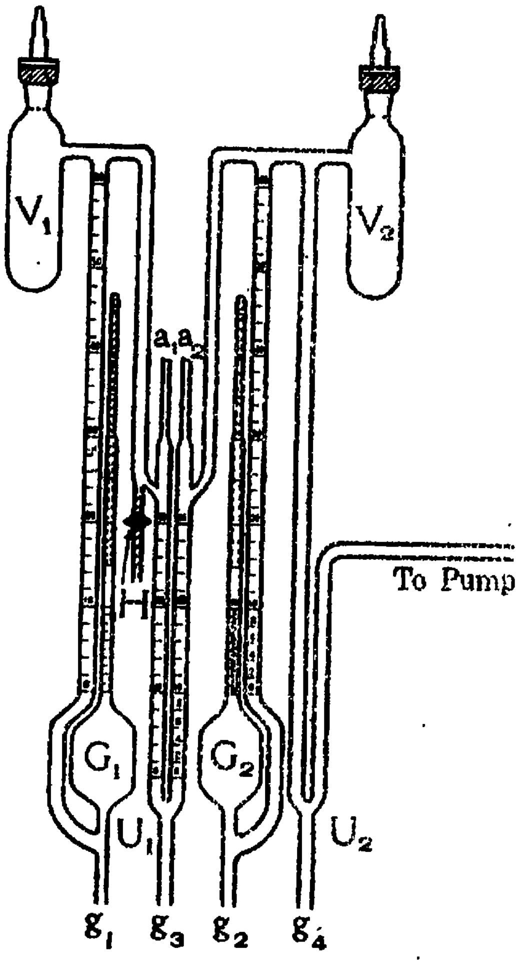

Fig. 23.—Knudsen's apparatus.

Procedure.—The tap H is opened and the experimental gas allowed to fill the reservoirs V_1 and V_2. Next the mercury in the tubes g_3, g_4 is allowed to fall below the bends of the U-tubes U_1 and U_2 and the pump set in action till the whole apparatus is evacuated to the desired pressure p_1. Then mercury is allowed to rise in g_3 nearly up to a_1, a_2 and the reservoir V_1 cut off from the rest of the apparatus. The pressure p_1 in V_1 is read by G_1 in the usual way. Then V_2 is further evacuated to the pressure p_2 and mercury is allowed to rise in g_4 above the bend in U_2 thereby cutting off the pump. The pressure p_2 of the gas in V_2 is read by G_2. Then mercury is allowed to fall in U_1 to some point above the bend in U_1 so that the two vessels V_1, V_2 can communicate through the capillary tube between a_1, a_2. After the gas has passed for some time mercury is allowed to rise in g_5 nearly up to a_1, a_2 thus stopping communication between V_1 and V_2 and the final pressures in V_1 and V_2 are again read on G_1 and G_2. Knowing these pressures initially and finally and the volumes of the reservoirs V_1 and V_2 and their connecting tubes, the amount of gas flowing from V_1 to V_2 can be easily calculated.

3·53. Discussion of the Results.—We discuss below the data of a particular experiment of Knudsen on the flow of carbon-dioxide through a bundle of 24 capillary tubes. The values of the constants of the apparatus were as follows :—r_1, the radius of the capillary = 0·00333 cm., l_1, the length of the tube = about 2 cm., temperature 25°C (average), λ, the mean free path = $6{\cdot}6 \times 10^{-6}$ cm. at 760 mm. η, the viscosity for $CO_2 = 1538 \times 10^{-7}$. The value of λ/r in this experiment varied from 1/160 to about 10^4. Knudsen's experimental results are shown in Fig. 24. The ordinates represent $\log T_0$ where $T_0 = M^*/\rho_0(p_1 - p_2)$, ρ_0 being the density of the gas measured at a pressure of 1 dyne. Thus T_0 represents the volume of gas flowing out per unit difference of pressure, measured at a pressure of 1 dyne. The abscissa represents $\log \lambda/r$.

λ is inversely proportional to pressure and hence the portion of the curve on the right corresponds to extremely low pressures. It will be seen from the curve that the quantity of gas flowing out at ordinary pressures decreases with decrease of pressure (AB) in accordance with Poisseuille's law, but after a time the decrease is less rapid (BC) in agreement with the result of Kundt and Warburg. With further decrease of pressure the flow increases (CD) and finally at very low pressures it becomes constant (DE). The portion DE represents the molecular streaming which is explained by the theory developed by Knudsen.

Knudsen found that his entire curve was best represented by a formula of the type

$$T_0 = ap + b\,\frac{1 + c_1 p}{1 + c_2 p}, \qquad \text{. . . . . (116)}$$

where a, b, c_1, c_2 are constants. The values of these constants which fit the curve given in Fig. 24 can be easily found by the method of least squares. These will be termed the *observed values*.

To find the significance of these constants we note that for large values of p, equation (116) yields $T_0 = ap$. Further Poisseuille's law must hold in this region. Hence 'a' of the empirical equation must equal $\pi r^4/8\eta l$. Knudsen thus calculated 'a' for the tube under discussion to be $3{\cdot}69 \times 10^{-6}$, while '$a$' observed is $3{\cdot}658 \times 10^{-6}$.

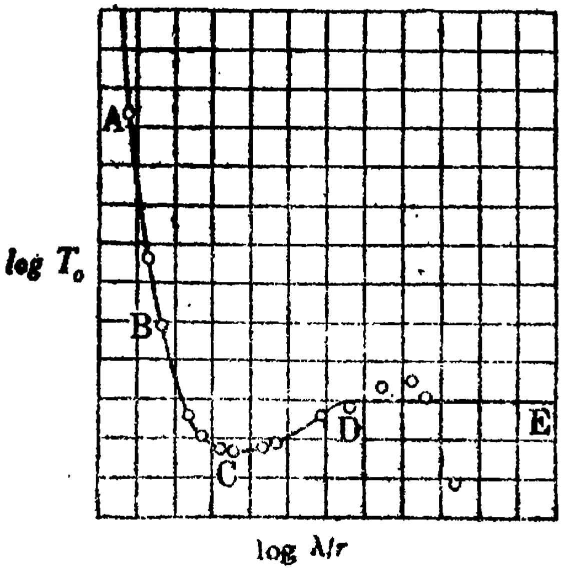

Fig. 24.—Curve showing the variation of rate of flow with mean free path.

Again for very small values of p, the first term can be neglected and $T_0 = b$ (constant). This is shown by the horizontal portion DE, of the curve and is the region of molecular streaming investigated by Knudsen. He found that the value of b as calculated from the relation $b = \frac{4}{3}\sqrt{\frac{2\pi}{\rho_0}}\frac{r^3}{l}$ was 0·0350, while the observed value of b was 0·0349. This confirms Knudsen's theory.

When the mean free path is small compared to the radius of the tube but not negligibly small, the formula reduces to

$$T_0 = ap + b\frac{c_1}{c_2} \quad . \quad . \quad . \quad . \quad . \quad (117)$$

This corresponds to the bend of the curve and represents the region investigated by Kundt and Warburg. To deduce c_1, c_2 we substitute the values of a, b in (117) and get the value of c_1/c_2. Further $c_2 - c_1$ can also be obtained, though in a complicated way, and hence c_1, c_2 can be found separately. Knudsen, partly from theoretical and partly from empirical considerations, gave the value

$$c_1 = 2\cdot 00\frac{\sqrt{\rho_0}}{\eta}r; \quad c_2 = 2\cdot 47\frac{\sqrt{\rho_0}}{\eta}r.$$

The agreement between the observed and the calculated values for various gases and tubes is very close, thereby confirming Knudsen's theory. The full expression is

$$T_0 = \frac{\pi r^4}{8\eta l}p + \frac{4}{3}\sqrt{\frac{2\pi}{\rho_0}}\frac{r^3}{l}\frac{(1+2\cdot 00\sqrt{\rho_0}\,rp/\eta)}{(1+2\cdot 47\sqrt{\rho_0}\,rp/\eta)} \quad . \quad . \quad . \quad (118)$$

3.54. Practical Applications of the Principles of Effusion.—The fact that the velocity of effusion depends on the molecular weight is utilized in mines for detecting the presence of the dangerous methane gas. A vessel fitted with a manometer and an arrangement for giving alarm is filled with air and closed by means of a porous plate of gypsum. If CH_4 (molecular weight 16) is present, it passes into the vessel by effusion thereby increasing the pressure and setting the alarm arrangement in action. Usually the vessel is a rubber globe with a metal band round its equator. It can, therefore, expand along the pole thereby acting on the alarm.

The phenomenon of effusion has been utilized by Knudsen and others for determining the saturated vapour pressure of substances which can be volatilized with difficulty such as mercury, lead, etc. The vapour of the substance is allowed to effuse through a small opening into a vessel which is highly evacuated and is in addition surrounded by a cooling arrangement. Thus the vapour of the substance is at once condensed and the pressure p' in the outer vessel is almost zero. Knowing the amount of vapour escaping out, the vapour pressure can be calculated. For details see Chapter XI.

There is another very important application of the phenomenon of effusion to the interesting problem of the separation of isotopes. The reader is probably aware that at the present time, it has been definitely proved that the atomic weight is not a distinctive property of elements. Most elements have been found to consist of atoms which possess identical chemical and physical properties, but differ in their atomic weight by small integral numbers. Thus ordinary neon has been found to consist of about 90 per cent of atoms having the atomic weight 20 and 10 per cent of atoms having the atomic weight 22. The isotopes of Cl have the weights 35 (75 per cent), 37 (25 per cent), and 39 (very small percentage). For a full list, see Aston's *Isotopes*.

As the isotopes have the same chemical properties, they cannot be separated by the usual methods of group separation used in chemistry. So various physical methods have been suggested for separating an element into its isotopic constituents. It is easily seen that if the gas is confined in a chamber and allowed to leak out through clay pipes possessing fine pores into an outer chamber, the gas in the second chamber will be richer in the lighter constituent, for the rate of leakage of molecules is $\sqrt{m_2/m_1}$ times faster for it, where m_2 denotes the mass of the heavy isotope and m_1 that of the light isotope. If the mole fractions of the two isotopes in one chamber be N and $1-N$, and in the other chamber n and $1-n$, the separation factor α is defined by the relation $\alpha = \frac{R}{r} = \frac{N}{1-N} \Big/ \frac{n}{1-n}$, where R and r are the ratios of molecular abundance. We further define the equilibrium separation factor α_0 as the instantaneous value of the separation factor when a differential quantity of material is allowed to diffuse from one chamber to another so that the composition of the first chamber is not altered. For the gaseous diffusion process $\alpha_0 = \sqrt{m_2/m_1}$, since $n/(1-n)$ does not alter and $N \propto n/\sqrt{m_1}$, $1-N \propto (1-n)/\sqrt{m_2}$.

Thus for a mixture of $U^{238}F_6$ and $U^{235}F_6$ molecules of molecular weight 352 and 349 respectively, $\alpha_0 = \sqrt{352/349} = 1{\cdot}0043$. In an actual process the conditions are far from equilibrium due to flow of the gas and in consequence, the effective separation factor α is still smaller. Therefore for utilising the process a large number of such *stages* has to be used in a *cascade*, when the abundance ratio for the sth. stage is $R_s=\alpha^s R_0$, R_0 being the initial abundance ratio.

Though the idea is quite straightforward its practical realisation has been extremely difficult but G. Hertz[1] succeeded in devising a mechanical contrivance based on the above principle by which he was able to separate the isotopes of neon very effectively. He used a battery of 24 diffusion pumps, and passed the gas through 48 clay pipes of special design on the principle of regenerative separation as shown schematically in Fig. 25. The clay pipes S_1, S_2 (shown shaded in the figure) are enclosed within outer glass tubes B_1, B_2...having side openings. The clay pipes are connected among themselves by glass tubes. The pumps P_1, P_2 .. are connected as shown in the diagram. V_h and V_l are two vessels in which ultimately the heavy and light constituents are separated. To start with, the gas is contained in V_h and the pumps are set in action. Consider the portion of the gas entering at A. Due to the action of the pumps it will be driven towards S_5 from where a portion richer in the lighter constituent will effuse out and will be sucked in by the pump P_3 and delivered into S_7. Here again a part, still richer in the lighter component, will effuse out and be delivered into V_l. Thus the portion travelling towards the right becomes richer and richer in the lighter component. The gas passing from S_7 to S_6 will be richer in the heavier component. Effusion will take place in S_6 and thus the gas passing to S_5 will be still richer in the heavier component. Thus the gas as it travels to the left becomes richer and richer in the heavier component. Hence the gas collecting in V_h will be richer in the heavier component and that in V_l richer in the lighter component. The process is, however, cyclic and repeats itself. The gas from V_l will travel to the left, the parts effusing from S_8 and S_7 will be still richer in the lighter component. Similarly from V_h the lighter component will escape faster through S_1 and the portion left in will be still richer in the heavier component. Hence as time

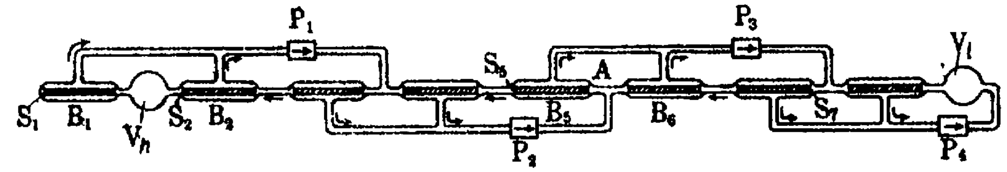

Fig. 25.—Schematic diagram of Hertz's apparatus for separation of Isotopes.

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[1] *Zeits. f. Physik*, **79**, 108, 1932.

elapses the separation of the two components becomes more and more complete. The flow of the gas in different parts of the apparatus is indicated by the arrows.

A slightly modified apparatus based on the same principle was employed by Hertz and his pupils who succeeded[1] in twenty hours in getting a mixture in which the proportion of Ne^{22}: Ne^{20} was 2·5 : 1 as compared to 1 : 9 in the ordinary mixture. Wooldridge and Smythe[2] separated in this way the gaseous isotopes of nitrogen and methane. The method was used on a very large scale by the U. S. A. physicists during the Second World War for separating U^{235} from U^{238}, U^{235} being the active isotope which undergoes fission on exposure to slow neutrons. Uranium hexafluoride, which is a gas, was used, with an initial abundance of 0·71% $U^{235}F_6$. If it is desired to produce 99% U^{235}, the number of stages required will be

$$s = \log (R_s/R_0)/\log \alpha = \log \frac{99/1}{0 \cdot 71/99 \cdot 3} \bigg/ \log 1 \cdot 0043 = 2436.$$

Actually since α is smaller, a still larger number of stages will be necessary. This is a colossal engineering problem but was successfully solved by the Americans who erected nearly 4000 diffusion stages at Oak Ridge in 1944 at a cost of 500 million dollars. For further details see *Theory of Isotope Separation* by K. Cohen, National Nuclear Energy Series, Division III, Vol. I B; or Smythe, *Atomic Energy*.

3·55. Applications of the Principles of Molecular Flow.—The flow through tubes at very low pressures investigated in §3·51 is of great practical importance. We have seen that the mass of gas escaping per second through a tube of circular cross-section is

$$M^* = \frac{4}{3}\sqrt{\frac{2\pi}{\rho_0}} \cdot \frac{r^3}{l}\,(p_1 - p_2)\rho_0.$$

But $\rho_0 = M/RT$. Hence the number of mols of gas escaping per second is

$$\frac{dn}{dt} = \frac{M^*}{M} = \frac{4}{3} \cdot \frac{r^3}{l}\sqrt{\frac{2\pi}{MRT}}\,(p_1 - p_2). \qquad . \quad . \quad (119)$$

Numerical calculation using (119) shows that the amount of flow through fine tubes at pressures of the order of 0·1 mm. into another chamber which is highly evacuated ($p_2 = 0$) is so small that it can be easily pumped by a good pump. This fact is of great importance in the investigation of positive rays which must be generated in gas-filled space, but investigated in complete vacuum. An experimental result may be quoted from Knudsen. Two vessels, each of 2¾ litres capacity, are connected by a tube of length 30 cm. and radius 0·1 mm. The one contains hydrogen under 0·01 mm. pressure, while the other is very highly evacuated. It is after 15 hours that one-third of the total quantity passes over to the evacuated vessel.

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[1] *Zeits. f. Physik*, **82**, 589, 1933.

[2] *Phys. Rev.*, **50**, 233, 1936.

From equation (119) we see that the 'resistance' of a tube to the flow of gas varies as l/r^3. This fact must be always borne in mind when connecting a vessel to a good vacuum pump for the purpose of evacuation. The tube connecting the vessel to the pump must have small resistance so that the high speed or pumping capacity afforded by modern pumps may be fully utilised. In other words, the limiting flow through the tube per second must be at least equal to the amount of gas pumped out per second. If it be less than the latter, the pump is unable to work to its full capacity. It is obvious from the formula that changes in r are much more effective than changes in l. To give a concrete idea, the following figures may be mentioned. With a Gaede molecular pump a connecting tube of 1 metre length must have an internal diameter of 20 mm. at least.

3·56. Theory of Gaede Molecular Pump.—The foregoing properties of highly rarefied gases have been utilized by Gaede[1] in designing a very efficient pump, called the molecular pump. This consists, as shown in Fig. 26, of a drum rotating within an outer cylinder with very small clearing space between the two except for a short length between m and n where the clearance space is larger. At m and n let us connect tubes leading to a manometer M. At low pressures the mean free path is large compared with the width of the clearance space, and hence molecular collisions are negligible and reflection from the surface is the dominating factor. As we have seen in §3·51 the impact and rebound of the molecules is equivalent to their conden-

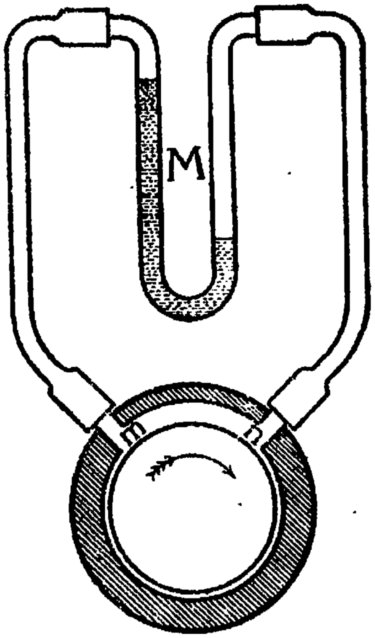

Fig. 26.—Gaede's molecular pump.

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[1] *Ann. d. Physik*, **41**, 337, 1913.

sation and subsequent evaporation from the wall in random directions. Thus when the inner cylinder rotates as indicated at a very high speed so that the velocity of the surface is comparable with the velocity of the molecules, the molecules coming from m are directed towards n by their impact and rebound from the drum as they remain in contact with the drum for a small time and are carried forward by it. The molecules coming from n are almost completely prevented from moving towards m. Further, the quantity of gas escaping from n to m through the narrow canal is quite negligible as shown in §3·55. Hence in this way a pressure difference is set up and maintained between m and n as indicated. The case is slightly different from the case of flow through tubes. In case of tubes the pressure difference causes a flow of gas through the tube; here the movement of the walls produces the pressure drop.

We can easily calculate an expression for the pressure difference set up between m and n. The molecules striking the rotating cylinder acquire by impact a velocity component parallel to the surface of the cylinder in the direction mn as explained above. Assume that the drift velocity of the gas due to this cause is u. Evidently u will depend upon the speed of rotation of the inner cylinder and will increase with the increase of this speed. Then from the discussion given in §3·51, we have for the volume of gas flowing out, using the same notation as before, $T_0 = b$, where b is a constant depending upon the dimensions of the space mn and will be given by an expression analogous to (114). Let us calculate the dependence of this T_0 on the drift velocity u; we have

$$b = \frac{M^*}{\rho_0(p_1-p_2)} = \frac{A\rho u}{\rho_0(p_1-p_2)} = \frac{Apu}{p_1-p_2}, \quad . \quad . \quad . \quad (120)$$

where A is the cross-sectional area of the opening and p the mean pressure of the gas. Therefore

$$p = \tfrac{1}{2}(p_1+p_2),$$

hence (120) yields

$$\frac{p_1+p_2}{p_1-p_2} = \frac{2b}{Au},$$

or

$$\frac{p_1}{p_2} = \frac{1+Au/2b}{1-Au/2b}. \quad . \quad . \quad . \quad (121)$$

Thus the ratio p_1/p_2 is independent of the gaseous pressure and increases with the increase of u and hence also of w_0, where w_0 is the linear velocity at the extremity of the inner cylinder. For a fixed u, p_1/p_2 must be constant. In practice a number of such arrangements in series are used. Table 4, obtained from a typical experiment, shows that p_1/p_2 does not even approximately remain constant and appears to pass through a maximum. The cause of this departure lies in the emission at low pressures of the gases adsorbed by the walls of the system to be evacuated which tends to counteract the diminution in p_2.

Table 4

n revolutions per min.	p_1 in mm.	p_2 in mm.	p_1/p_2
12000	0·05	$2\cdot10^{-7}$	$250\cdot10^3$
12000	1·00	$5\cdot10^{-6}$	$200\cdot10^3$
12000	10·00	$3\cdot10^{-5}$	$333\cdot10^3$
12000	20·00	$3\cdot10^{-4}$	$66\cdot10^3$
6000	0·05	$2\cdot10^{-5}$	
2500	0·05	$2\cdot10^{-4}$	

When the pressure is so high (above about 20 mm.) that the mean free path is negligibly small compared with the width of the space, the mechanism is quite different. In this case molecules coming from m and n suffer collision with other molecules and viscous forces are brought into play. It can be shown from the kinetic theory that for this case

$$p_1-p_2=\frac{6\eta w_0 l}{h^2}, \qquad (122)$$

where η is the viscosity of the gas, l the length of the space mn, and h the width of the space. Thus the pressure difference is very small and is independent of the mean pressure of the gas.

It is for these reasons that this pump can only be used in conjunction with an auxiliary pump which will produce pressures of the order of 0·1 mm. The fore-pump is connected at n and the vessel to be evacuated is connected at m. Of course the speed of the pump depends upon the pressure developed by the fore-pump.

In recent years the mechanical design has been considerably improved by Holweck and Siegbahn. In Holweck's design the cylinder contains two spiral grooves cut on it, symmetrically starting from the high vacuum nozzle m which is in the middle. The grooves are at first deep, but gradually become shallower and finally disappear when the edges of the cylinder are reached. The drum is rotated in the vacuum by an induction motor worked by diphase current.

3·57. Dushman Manometer.—This consists of a horizontal disc suspended by a quartz fibre carrying a mirror for the purpose of measuring the rotation of the system. Parallel to this disc there is a second disc placed a few millimetres below the first one and is capable of rotating at high speed about the quartz fibre as axis. If the whole system is suspended in a gas at very low pressure and the lower disc rotated from outside by means of a magnet, the fixed disc will be rotated through an angle which will depend upon the velocity of rotation of the lower disc and the pressure of the gas. Thus a knowledge of the deflection gives the pressure of the contained gas.

To deduce the formula we make use of equation (111) which gives the force exerted by the rotating disc on the fixed disc per unit area of the former taken at a place where the linear velocity is v. But $v = r\omega$ where r is the distance of the element from the axis and ω is the velocity of rotation. Hence the moment of the forces exerted on the fixed disc is

$$\int_0^a \frac{3\pi}{32}\,\rho\bar{c}\,.\,r\omega\,.\,r\,.\,2\pi r\,dr = \frac{3\pi^2}{16}\,\rho\sqrt{\frac{8RT}{M\pi}}\,\frac{a^4}{4}\omega = c\theta,$$

where c is the couple per unit twist. Thus θ is proportional to $p\omega$. The value of the numerical coefficient is, however, uncertain. In practice therefore the instrument is calibrated by actual comparison with another manometer.

3·58. Thermal Transpiration.—So far we considered such phenomena in which the temperature was uniform throughout the gas. We shall now study such low pressure phenomena in which the temperature is different in different parts. The simplest case is that of thermal transpiration.

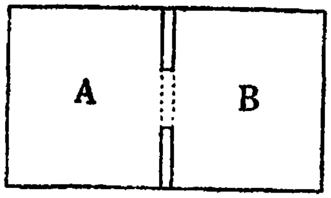

Fig. 27.—Thermal transpiration.

Let there be two chambers A and B (Fig. 27) containing a certain gas at different temperatures. Denote these temperatures by T_A and T_B and assume that $T_A > T_B$. The two chambers communicate with each other through a porous plug (shown dotted in the figure) or, better, through a narrow opening of *negligible thickness.* If initially the pressures in the two chambers are equal, and n_A, n_B denote the initial molecular densities in A and B respectively, we have from the gas law $p = nkT$, that $n_A/n_B = T_B/T_A$. The efflux of the gas from A will be, as proved in §3·49, $\frac{1}{4}mn_A\bar{c}_A$ and that from B, $\frac{1}{4}mn_B\bar{c}_B$. Now

$$\frac{n_A\bar{c}_A}{n_B\bar{c}_B}=\frac{T_B}{T_A}\sqrt{\frac{T_A}{T_B}}=\sqrt{\frac{T_B}{T_A}}$$

and $T_B < T_A$, hence $n_A\bar{c}_A < n_B\bar{c}_B$. Therefore there is a net transfer of some gas from B to A, *i.e.*, from the colder to the hotter chamber. Now the pressures in the two chambers were initially equal, thus the pressure in the hotter vessel tends to increase over that in the colder one. This case differs from the ordinary case of effusion where the temperature is equal and the transfer is caused by the difference in pressure. Here difference in temperature is the cause of transfer. This phenomenon[1] is called *thermal effusion* or *thermal transpiration* and was first investigated by Osborne Reynolds.[2]

This net transfer will continue and the molecular density and pressure in the hotter vessel will go on increasing till finally a steady state is attained when the efflux from both sides becomes equal. If we denote the final pressures and molecular densities for the two chambers by p_A, p_B and n_A, n_B respectively, then for equilibrium the condition of equality of flux gives

$$n_A\bar{c}_A = n_B\bar{c}_B.$$

Now $n_A = p_A/kT_A$ and $\bar{c}_A \propto \sqrt{T_A}$, and similarly for n_B and $\bar{c}_B$. Hence on substitution we obtain

$$\frac{p_A}{p_B}=\sqrt{\frac{T_A}{T_B}}, \qquad \text{. . . . . . (123)}$$

i.e., the final thermo-molecular pressures are in the ratio of the square roots of the absolute temperatures.

The phenomenon of thermal transpiration was experimentally investigated by Reynolds.[3] His apparatus consists essentially of two chambers separated by a plate of porous material. Arrangements were made for keeping the chambers at constant but different temperatures for hours, also for measuring the pressure of the gas and for exhausting the chambers. In most of his experiments he maintained the gas in the two chambers at 8°C. and 100°C. The porous plug was made of biscuit-ware, meerschaum or stucco. The theoretical relation was found to hold approximately, but departures were observed at high pressures. In fact the foregoing considerations are applicable only when the gas is at very low pressure, *i.e.*, λ is large compared with the length and the radius of the numerous capillaries to which the porous plug is equivalent. Using 10 tubes each having constrictions and heated to 500°C., Knudsen obtained a pressure in one vessel equal to 10 times that in the other. In the case of such tubes, as distinguished from the case of holes of negligible thickness, the phenomenon is different from the one theoretically discussed above. It is the case of flow through a tube produced by a temperature gradient alone without any imposed pressure gradient. At very low pressures, *i.e.*, in the case of molecular flow, the phenomenon can be studied in a manner somewhat similar to that of §3·51. Theoretical investigations show that for the condition of zero flow through tubes of circular cross-section $p/\sqrt{T}$ is constant along the tube. If the dimensions of the connecting tubes or capillaries are not negligibly small compared with λ, we must, while considering the flow along these tubes, take into account the viscosity, radius of the tube, its length, etc. Knudsen[1] worked out a theory for this case and found the experimental results to agree with the theory. For details the original paper should be consulted.

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[1] A fine illustration of the phenomenon of thermal transpiration is furnished by the following experiment :—Take a porous clay vessel (having pores of the order of 10^{-5} cm.) provided with an arrangement for heating the enclosed air and immerse it completely in water. When the enclosed gas is heated the cold atmospheric air can be seen bubbling through the water after which it enters the clay vessel. For a vessel of capacity 100 c.c. and with strong heating arrangements 100 c.c. of gas can be made to enter the vessel per minute.

[2] Osborne Reynolds, *Scientific Papers*, Vol. 1, p. 257; or *Phil. Trans*. Part II (1879).

[3] Osborne Reynolds, *Scientific Papers*, Vol. 1, p. 265.

3·59. Thermal Conduction in Rarefied Gases.—Like viscosity, thermal conduction in a gas can also be treated at ordinary, intermediate and very low pressures. The case of ordinary pressure was treated in § 3·39. At intermediate pressures we have, analogous to the viscous slip, a *temperature jump* or discontinuity at the wall, the temperature jump distance g being directly proportional to the mean free path. A theory of the temperature jump can be developed in terms of the interaction of molecules with the surface just as the value of ζ in terms of f was found in § 3·50. We shall, however, concern ourselves only with the phenomena at very low pressures when the mean free path is large compared with the linear dimensions of the contained gas.

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[1] *Ann. d. Physik*, **31**, 205, 1910; **33**, 1435, 1910, or see Loeb, *Kinetic Theory of Gases*, (1934), pp. 355—364.

The transfer of heat through a gas at low pressure was investigated experimentally by Knudsen[1], and Soddy and Berry[2] and a theory of the phenomenon was given by Knudsen[3] and Smoluchowsky. The experiment consists in studying the transfer of heat from a hot plate to a cold plate or from a thin cylindrical wire to a concentric hollow cylinder, the space between the two being filled with the experimental gas. As a result of these experiments the conductivity of a gas was found to decrease with decrease of pressure at extremely low pressures. As in the case of free-molecule viscosity, this is due to the mean free path becoming very large when molecular collisions become rare and the phenomenon is therefore called free-molecule or molecular heat conduction. Knudsen's theory of the phenomena is very similar to his theory of the transfer of momentum given in § 3·51 and is given below.

Let the two surfaces A, B be maintained at temperatures T_1, T_2 and further, let us make the simple assumption that the molecules leaving a surface have acquired its temperature, so that the molecules reaching and leaving A carry the mean energy of a Maxwellian gas corresponding to temperatures T_2 and T_1 respectively. The number of molecules of the velocity c_2 striking unit area of A per second is, from equation (109), equal to $2n_2\pi a^3 e^{-bc_2^2} c_2^3\, dc_2$ where n_2 is the number density of molecules moving towards A. We have put here 2 instead of 1 in (109) since n_2 represents the density of molecules moving towards one side only or just half the density in the equivalent Maxwellian gas. The translational energy carried by every one of them is $\frac{1}{2}mc_2^2$. Hence the total energy imparted to unit area of A per second is

$$E_2 = \int_0^\infty \tfrac{1}{2}mc_2^2 . 2n_2\pi a^3 e^{-bc_2^2} c_2^3\, dc_2 = \tfrac{1}{4}n_2\bar{c}_2 . 2kT_2, \quad . \quad . \quad (124)$$

a result which could be directly written from problem 1 of §3.49. Similarly the energy leaving the surface of A per unit area will be $E_1 = n_1\bar{c}_1 . kT_1$. Hence the rate of loss of translational energy by A is

$$n_1\bar{c}_1kT_1 - n_2\bar{c}_2kT_2.$$

Now the number of molecules moving in one direction between the plates must equal those moving in the other direction since there is no accumulation between the plates. Hence $\frac{1}{2}n_1\bar{c}_1=\frac{1}{2}n_2\bar{c}_2$, and this must also equal $\frac{1}{4}n\bar{c}$ where n denotes the total molecular density and $\bar{c}$ the mean speed of the gas molecules between the plates, n being equal to n_1+n_2. Hence the expression for loss of translational energy becomes

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[1] *Ann. d. Physik*, **34**, 593, 1911; **6**, 129, 1930.

[2] *Proc. Roy. Soc.*, **83**, 254, 1910; **84**, 576, 1911.

[3] *Ann. d. Physik*, **35**, 983, 1911.

$$\tfrac{1}{2}n\bar{c}.\ k(T_1-T_2).$$

If the molecule possesses energies of rotation and vibration also, the loss of energy due to this cause will be given by

$$\tfrac{1}{4}n\bar{c}(E_{r_1}-E_{r}\ ),$$

where E_{r_1} and E_{r_2} denote the energy of the molecule, other than translational, at temperatures T_1 and T_2. Hence the total loss of energy becomes

$$\tfrac{1}{2}n\bar{c}.\ k(T_1-T_2)+\tfrac{1}{4}n\bar{c}(E_r-E_{r_2}). \quad . \quad . \quad . \quad (125)$$

Since $$\gamma=\frac{c_p}{c_v}=\frac{E_t+E_r+kT}{E_t+E_r};\quad E_t=\frac{3}{2}kT,$$

we have $$E_r=\frac{5-3\gamma}{\gamma-1}\times\tfrac{1}{2}kT.$$

Further, $$\bar{c}=\sqrt{8RT/M\pi}\ ;\ p=nkT,$$

where T denotes the temperature[1] corresponding to $\bar{c}$ for a Maxwellian gas and p its pressure. Hence the total loss of heat energy Q from unit area of A is given by

$$Q=\tfrac{1}{4}p\sqrt{\frac{2R}{M\pi}}.\frac{\gamma+1}{\gamma-1}.\frac{T_1-T_2}{\sqrt{T}}\text{ ergs.} \quad . \quad . \quad (126)$$

We thus see that conduction of heat under these conditions follows laws quite different from those at ordinary pressures. It is seen to be independent of the distance between the plates and is proportional to the pressure of the gas.

Experimentally it was found that the loss of heat was proportional to the temperature difference T_1-T_2 and to the pressure but was less than that given by (126). To explain this Knudsen, following Smoulchowski, assumes that the molecules leaving the plate have not acquired its temperature; they adjust themselves only through a fraction a of the difference of temperature between the plate and their own before collision. Knudsen calls this quantity a, the *accommodation coefficient*, which denotes the fractional extent to which the molecules, on suffering encounter with the wall, get their mean energy adjusted or accommodated towards the mean energy which would be possessed by molecules of a gas at the temperature of the wall. Thus if E_i, E_r denote the mean energy of the incident and reflected molecule and E_w that corresponding to the wall temperature we have

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[1] T can be obtained from the relations $\frac{1}{2}n_1\bar{c}_1=\frac{1}{2}n_2\bar{c}_2=\frac{1}{4}n\bar{c}$, and $n=n_1+n_2$. Since $\bar{c}\propto\sqrt{T}$, this yields $1/\sqrt{T}=\frac{1}{2}(1/\sqrt{T_1}+1/\sqrt{T_2})$, or if we take the accommodation coefficient into account, we get $1/\sqrt{T}=\frac{1}{2}(1/\sqrt{T_1'}+1/\sqrt{T_2'})$. If the gas outside the plates has a temperature T' different from that of the gas between the plates we evidently have $p'/p=(T'/T)^{\frac{1}{2}}$.

$$E_r - E_i = a\,(E_w - E_i), \quad . \quad . \quad . \quad . \quad (127)$$

or since E is proportional to T,

$$T_r - T_i = a\,(T_w - T_i), \quad . \quad . \quad . \quad . \quad (128)$$

Assuming a to be the same for both the plates and denoting the temperatures of the molecules leaving the plates T_1, T_2 by T_1', T_2' we have

$$T_1' - T_2' = a\,(T_1 - T_2')\,; \;\; T_2' - T_1' = a\,(T_2 - T_1'), \quad . \quad (129)$$

whence

$$T_1' - T_2' = \frac{a}{2-a}(T_1 - T_2), \quad . \quad . \quad . \quad (130)$$

It is evident that in the foregoing transfer equation (125) we must have $T_1' - T_2'$ in place of $T_1 - T_2$. Knudsen devised some ingenious experiments from which he concludes that the accommodation coefficient is, within limits of experimental error, the same for translational energy as for other forms of energy. Hence (126) becomes modified into

$$Q = \frac{1}{4}\,\frac{a}{2-a}\,p\sqrt{\frac{2R}{M\pi}}\;\frac{\gamma+1}{\gamma-1}\;\frac{T_1 - T_2}{\sqrt{T}}. \quad . \quad . \quad . \quad (131)$$

From equations (126) and (131) it is evident that the transfer of heat is proportional to the pressure. This is the principle upon which the action of the Pirani vacuum gauge depends. In this a constant current flows through a lamp filament. The filament attains a steady temperature and hence a constant resistance which depends upon the loss of heat through the gas by conduction and hence from equation (126) or (131) upon the pressure of the enclosed gas. Thus from a knowledge of the resistance the pressure can be found.

3·60. Nature of the Accommodation Coefficient.

—The accommodation coefficient can be experimentally determined[1] by measuring the heat loss from a plate and then utilising eqn. (131). It is found to depend very largely on the temperature, the cleanness of the solid surface, etc. and decreases steadily as the temperature is lowered. All values of a from 0 to 1 seem to be possible. Attempts have also been made to calculate a from theoretical considerations. Assuming perfectly elastic collisions between spherical molecules of the gas and of the wall, of masses m and m' respectively, it can be shown from the laws of impact that

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[1] For full details see Loeb, *Kinetic Theory of Gases*, (1934), §80-81.

$$a = 1-\left(\frac{m-m'}{m+m'}\right)^2 . \quad . \quad . \quad . \quad . \quad (132)$$

The problem is really one of wave-mechanics and has been tackled on these lines by Jackson and Howarth[1].

3·61. Knudsen's Absolute Manometer.—From his study of the laws of heat transfer in gases at low pressure, Knudsen[2] was able to devise an absolute manometer for the measurement of extremely low pressures. The manometer is *absolute* because it gives the pressure directly in dynes and requires no preliminary calibration by comparison with a standard gauge. Its indications do not depend upon the nature of the contained gas.

The principle of the manometer will be best understood by reference to Fig. 28. B_1, B_2 are two movable plates suspended by a quartz fibre D carrying a mirror M. Opposite these plates are two fixed plates A_1, A_2, which are heated electrically and kept at a temperature above that of the cold plates B_1, B_2. When such a system is suspended in a rarefied gas, the gas molecules impinging on B from the side A possess greater momentum than the molecules impinging on the other side of B, and hence the vanes B_1, B_2 experience a force repelling them away from A_1, A_2, and are deflected. The deflection is measured by the lamp and scale method and depends upon the pressure of the contained gas. Thus knowing the deflection, the pressure of the contained gas is determined.

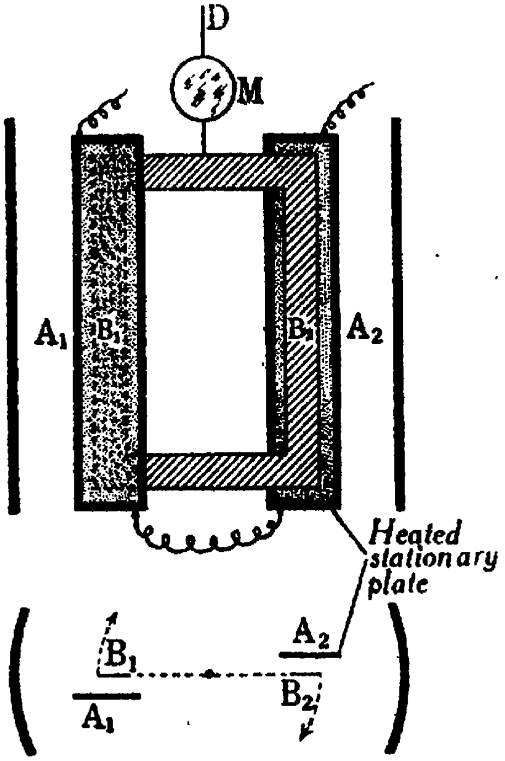

Fig. 28.—Knudsen's absolute manometer.

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[1] *Proc. Roy. Soc.*, **142**, 447, 1933.

[2] *Ann. d. Physik*, **32**, 809, 1910.

A theory of the apparatus has been given by Knudsen[1] which is however only applicable when the distance between the fixed and the movable plates is small compared to the mean free path of the gas, so that the molecules strike the one plate exactly in the same state in which they left the other. Also the dimensions of the plates are supposed to be large compared with the distance between them so that the edge effects can be neglected.

Let the temperature of the plates A and B be respectively T_1 and T_2 and let the average velocities and the mean square velocities of the gas molecules corresponding to these temperatures be $\bar{c}_1$, $\bar{c}_2$ and C_1^2, C_2^2 respectively. Suppose the molecular density between the plates of such molecules as move towards B is n_1 and of those moving towards A is n_2. If we assume that the molecules on striking the plate acquire its temperature, then they leave the plate as a Maxwellian gas having a velocity distribution corresponding to the temperature of the plate. The part of B facing A thus receives a momentum $\frac{1}{3}n_1mC_1^2$ per unit area due to impact of molecules coming from A since in this case the momentum will be only half of that given by equations (4) or (9) as proved in the footnote on p. 124, and n_1 corresponds to $\frac{1}{2}n$ here. Similarly B experiences a momentum $\frac{1}{3}n_2mC_2^2$ due to molecules leaving B. Hence due to the gas between the plates the total pressure repelling B is

$$\tfrac{1}{3}m\,(n_1C_1^2+n_2C_2^2).$$

Again if the molecular density outside the plates be n and the average velocity and mean square velocity be $\bar{c}$ and C^2 respectively, the plate B is forced towards A with a pressure p where $p = \frac{1}{3}mnC^2$. Hence the resultant force per unit area repelling the plates is

$$F = \tfrac{1}{3}m(n_1C_1^2+n_2C_2^2)-p. \quad . \quad . \quad . \quad (133)$$

Again as proved in §3·59, we have

$$\tfrac{1}{2}n_1\bar{c}_1 = \tfrac{1}{2}n_2\bar{c}_2 = \tfrac{1}{4}n\bar{c},$$

since there is no accumulation of gas between the plates or outside. Now, since C and $\bar{c}$ are proportional we have

$$n_1C_1 = n_2C_2 = \tfrac{1}{2}nC.$$

Hence (133) yields

$$F = \tfrac{1}{3}mn.\,\tfrac{1}{2}C(C_1+C_2)-p = \tfrac{1}{2}p\left(\frac{C_1+C_2}{C}\right)-p. \qquad (134)$$

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[1] *Ann. d. Physik*, **32**, 809, 1910. See also Smoluchowski, *Ann. d. Physik*, **35**, 1000, 1911.

If further the whole gas is kept at the temperature T_2 of the cold plate, $C = C_2$. Hence

$$F = \frac{p}{2}\left(\frac{C_1}{C_2} - 1\right) = \frac{p}{2}\left(\sqrt{\frac{T_1}{T_2}} - 1\right).$$

$$\therefore p = \frac{2F}{\sqrt{T_1/T_2} - 1} . \qquad (135)$$

If the difference between T_1 and T_2 is not large,[1]

$$p = 4F\frac{T_2}{T_1 - T_2} \text{ dynes/cm}^2. \qquad (136)$$

F can be evaluated from the deflection and the elastic constants of the apparatus and hence p the pressure of the gas can be calculated. It must be mentioned, however, that p includes the pressure of all vapours present in the system, including mercury vapour if any. The MacLeod gauge, on the other hand, does not measure the vapour pressure of mercury[2].

We have assumed above that the molecules acquire the temperature of the plate which they strike. As shown in §3·59 this is not so in general. Assuming the accommodation coefficient a to be the same for both the plates, the temperatures T_1', T_2' of molecules leaving the plates of temperatures T_1, T_2 respectively will be given by (129). Equation (129) on addition yields

$$T_1' + T_2' = T_1 + T_2, \qquad (137)$$

or since T is proportional to C^2 where C is the root mean square velocity, we have

$$C_1'^2 + C_2'^2 = C_1^2 + C_2^2. \qquad (138)$$

If the difference between C_1 and C_2 is small, equation (138) yields correct to small quantities of the first order,

$$C_1' + C_2' = C_1 + C_2. \qquad (139)$$

Now in this case we should have $C_1' + C_2'$ in place $C_1 + C_2$ in equation (134). Thus by virtue of equation (137) the expression obtained is the same as before, if we neglect small quantities of higher order, provided the temperature difference $T_1 - T_2$ is small.

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[1] This formula can be deduced in a very simple way by considering it as a thermal transpiration effect between the mean temperature $\frac{1}{2}(T_1 + T_2)$ inside the plates and T_2 outside. The pressure p_i between the plates is given by $p_i/p = \sqrt{\frac{1}{2}(T_1 + T_2)/T_2} = \sqrt{1 + (T_1 - T_2)/2T_2} = 1 + \frac{1}{4}(T_1 - T_2)/T_2$ approx. and $F = p_i - p$.

[2] For further details see Dushman: *Production and measurement of high vacua*.

A gauge based on the above principles can be employed to measure the lowest pressures yet attained. Woodrow[1] constructed a gauge on the same principle which, with a temperature difference of 100°C. between the plates, could be used to measure down to 3×10^{-8} mm. of mercury, while another modification by Shrader and Sherwood[2] could read to 5×10^{-9} mm. The gauge however cannot be employed above 10^{-3} mm. since the mean free path then becomes comparable with the distance between the plates.

3·62. Thermal Creep and the Radiometer.—Crookes (1870) devised an instrument called the radiometer which is used to measure the intensity of radiation falling on it. It consists of a number of thin vertical vanes of mica suspended at the ends of a light aluminium rod *r* inside a partially evacuated glass vessel (Fig. 29). Two such rods fixed at right angles are shown in the figure, and are capable of rotating about the vertical axis *a*. The outer face of the vanes is coated with lampblack while the inner faces are left clear. When radiation (thermal or light) falls on the blackened face the vanes begin to revolve in such a direction that the blackened face continually recedes from the source of radiation. This is called the *radiometer effect.*

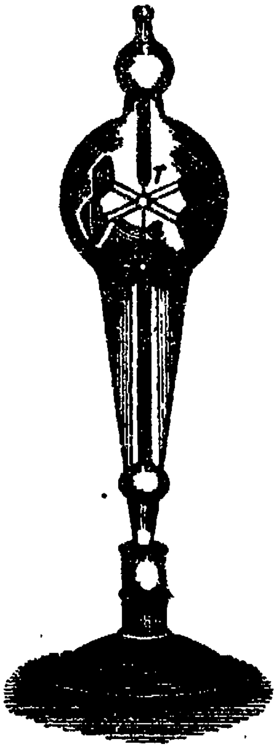

Fig. 29.
Crookes' radiometer.

The following simple explanation of the radiometer effect is often given but is hardly convincing. The blackened face absorbs the incident radiation and thereby its temperature is raised while the clear face remains at a lower temperature. The molecules striking the blackened face therefore become more heated than the molecules striking the other side of the vane and hence carry, on the average, greater energy and momentum. The consequence is that there is a net effective force repelling the vanes away from the incident radiation.

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[1] *Phys. Rev.*, **4**, 491, 1914.

[2] *Phys. Rev.*, **12**, 70, 1918.

A quantitative theory of the radiometer effect has been given by Hettner and Czerny, Einstein, Epstein[1] and others, following the ideas developed by Maxwell, and seems to be fairly well confirmed by experiments. According to this the radiation falling on the vane acts by heating the vane unequally so that a temperature gradient is established along the vane whose magnitude will depend upon the conductivity of the gas, conductivity of the vane, intensity of the radiation, the perimeter of the vane and also upon any convection currents that may be produced. The temperature gradient causes a *thermal creep* of the gas as pointed out by Maxwell, the gas moving towards regions of higher temperature. The existence of this creep motion can be easily explained. Molecules striking the surface obliquely and coming from hotter regions bring with them greater tangential momentum than those coming from the colder regions. Thus the surface delivers a tangential momentum to the gas directed towards the hotter regions, producing thereby a thermal creep from the colder to the hotter region. As a result of this thermal creep viscous forces are exerted and we have to solve the hydrodynamical problem of §3·51 with this boundary condition of the creep velocity which, when partially obstructed, will produce a pressure gradient. Thus the pressure on the hotter side of the vane increases on account of this thermal creep and deflects the vane away from the incident radiation. The quantitative calculations[2] are too complicated to be given here. We shall content ourselves by simply quoting the results for a thin flat circular disc. The difference of temperature $\triangle T$ between the centres of the two sides of the disc is found to be given by

$$\triangle T = \frac{2}{\pi} \frac{aI}{K_g + \frac{2a}{\pi d} K_d}, \quad . \quad . \quad . \quad . \quad (140)$$

where a, d and K_d respectively denote the radius, the thickness and the conductivity of the disc; K_g the conductivity of the gas and I the intensity of radiation for the case of a uniform beam of light. The radiometric force on the disc is found to be given by

$$F = -3\pi \frac{R\eta^2}{Mp} \triangle T,$$

where p is the pressure of the gas and η its viscosity, and $\triangle T$ is given by (140). For a non-conducting disc ($K_d = 0$), this reduces to

$$F = -\frac{6R\eta^2 aI}{Mp\,K_g}. \quad . \quad . \quad . \quad . \quad . \quad (141)$$

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[1] *Zeits. f. Physik*, **54**, 537, 1929.

[2] For detailed discussion see Loeb, *Kinetic Theory of Gases*, pp. 364-386 (1934).

F is seen to be proportional to the intensity of radiation I thereby explaining its use as a radiometer.

3·63. Value of Constants.—In Table[1] 5 a number of constants are given which serve to give an idea of the several magnitudes involved in the kinetic theory of gases. The gases are at 0°C. and atmospheric pressure.

Table 5

Gas	Mass of molecule $m \times 10^{24}$ gm.	Root mean square velocity in metres per sec.	Viscosity $\eta \times 10^6$ in gm.cm.$^{-1}$ sec.$^{-1}$.	Thermal conductivity $K \times 10^6$ in cal. cm.$^{-1}$ sec.$^{-1}$ °C^{-1}.	Mean free path $\lambda \times 10^6$ cm.	Molecular diameter $\sigma \times 10^8$ cm.
H_2	3·1	1839	86	318	18·3	2·47
N_2	43·1	493	166	52	9·44	3·5
O_2	49·2	461	187	56	9·95	3·39
He	6·1	1311	189	339	28·5	2·18
A	61·3	413	210	38·9	10·0	3·36
Cl_2	58·5	307	129	..	4·57	4·96

Problems—1. Calculate the number of molecules crossing unit area upwards with the vertical component velocity greater than u_0.

2. In an absolute manometer the temperatures of the two plates are 23·4°C and 31·7°C, the surrounding gas being maintained at the temperature of the cold plate. If the cold plate is repelled with a force of $1·6 \times 10^{-2}$ dynes/cm.^{2}, calculate the pressure of the gas.

BOOKS RECOMMENDED

A good elementary account of the subject-matter of this chapter will be found in Eugene Bloch, *Kinetic Theory of Gases*, English translation published by Methuen and Co., or in Jeans, *Kinetic Theory of Gases* C.U.P. (1940). For a more detailed account, Kennard, *Kinetic Theory of Gases*, (McGraw-Hill, 1938) is excellent.

OTHER REFERENCES

1. Jeans, *Dynamical Theory of Gases.*
2. Loeb, *Kinetic Theory of Gases*, 1934.

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[1] The table is largely taken from Kaye and Laby, *Physical Constants.* No great accuracy is claimed for the values given.

3. Meyer, *Kinetic Theory of Gases.*

4. Fowler, *Statistical Mechanics* (Camb. Univ. Press, 1936).

5. Chapman and Cowling, *The Mathematical Theory of Non-uniform Gases* (Camb. Univ. Press, 1952).

6. Hirschfelder, Curtiss and Bird, *Molecular Theory of Gases and Liquids* (John Wiley, 1954).

7. Grew and Ibbs, *Thermal Diffusion in Gases* (Camb. Univ. Press, 1952).

8. Clemens Schaefer, *Einführung in die theoretische Physik*, Vol. 2, Chap. VIII.

CHAPTER IV

HEAT ENGINES

4·1. Introduction.—We have seen in the last chapter that Heat is a kind of motion. Whenever motion disappears it reappears as heat, and experiments show that 1 calorie of heat is equivalent to $4 \cdot 18 \times 10^7$ ergs of work. The question naturally arises: "Can we not reverse the process? Can we not, by some contrivance, convert heat which is in so much excess about us, to useful work?" This is in fact the function of heat engines which we are going to discuss. They are contrivances for converting heat into work.

But the early investigators were profoundly ignorant of the "Nature of Heat", hence the problem did not present itself to them in this form. They however observed that whenever bodies get heated, they develop a capacity for doing mechanical work. We may take three examples familiar to everybody:—

1. When water is boiled in a closed kettle, the lid is blown off by steam generated inside. This shows that high pressure steam can be made to do work.

2. When gunpowder or any explosive is exploded a sudden impulse is created which may be utilised for throwing stones, cannon-balls and for breaking rock.

3. High velocity wind can be made to do work, *e.g.*, from early times sails have been used for the propulsion of ships, for driving mills (windmills). We know that such winds are due to intensive heating of parts of the earth's surface by the sun.

The three illustrations chosen above have served as the starting point for three different classes of engines which convert heat to work, *viz.*, (1) the steam engine widely used for locomotion and industry, (2) the internal combustion engines used in motor cars, aeroplanes, and for numerous other purposes, (3) the windmills and steam turbines.

Many of the principles utilised in these engines are common to all classes; we shall therefore begin the subject by a study of the Steam Engine[1]. The mechanical details are outside the scope of this book and will be given in the barest outline.

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[1] For an account of the evolution of the steam engine see the Authors' *A Text Book of Heat for Junior Students* (1954), or Ewing, *Steam Engine and other Heat Engines.*

4·2. Modern Steam Engines.—Since the time of its first inventor James Watt, many important innovations have been introduced into the steam engine though the main features remain the same. The essential parts of a *piston* or *reciprocating steam engine* are shown diagrammatically in Fig. 1.

Steam from the boiler enters the steam chest, also called the slide casing, in which usually a D-slide valve reciprocates. The valve slides upon a plane surface attached to the main cylinder. There are three holes bored in this surface, the upper and the lower holes leading to the upper and lower parts of the cylinder, while the middle hole communicates with the exhaust pipe leading to the condenser.

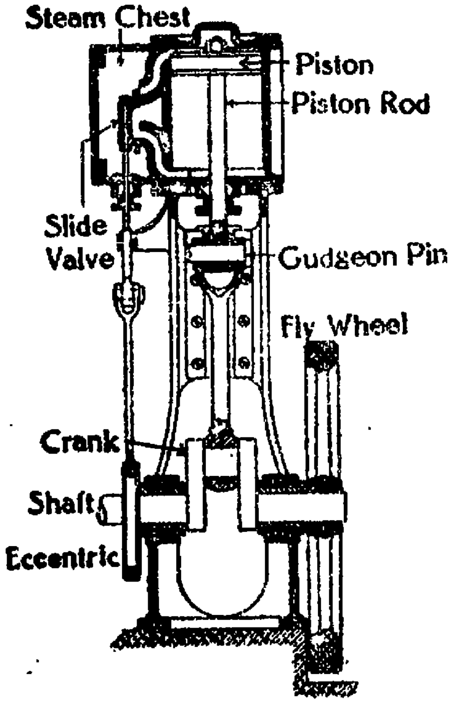

Fig. 1.—Main parts of a Steam Engine.

The slide valve is so mounted that with the slide in the position shown in Fig. 1, steam enters the cylinder at the top through the upper hole and pushes down the piston, the steam on the other side of the piston being thrown out through the lower hole, the cavity in the D-slide, and the middle hole to the exhaust pipe. When the piston has reached the end of its downward stroke, the D-slide takes up such a position that steam is allowed to enter through the lower hole and pushes the piston upwards, the steam above the piston being thrown out of the upper hole to the exhaust. This backward and forward motion of the piston is communicated to the piston rod which is constrained to move in a straight line by the gudgeon pin travelling between two guides. To the gudgeon pin is connected the connecting rod whose other end is jointed to the crank mounted on the crank shaft. Thus the to-and-fro motion of the piston is transformed into the rotational motion of the crank shaft and the flywheel. Upon the crank shaft is mounted the eccentric which is simply a circular disc so mounted that its axis of rotation does not pass through its centre. The eccentric rotates within a ring bearing, called the eccentric strap, which is attached to the eccentric rod, the rod being jointed at the other end to the valve spindle. The rotation of the Crank shaft thus produces backward and forward motion of the eccentric rod and the D-slide valve. The proper timing action of the slide valve is accomplished by so mounting the eccentric on the shaft that it is turned through 90° relative to the crank.

Watt used engines with low steam pressure but such engines are comparatively inefficient, as we shall presently see, and in modern times high pressure engines are largely employed necessitating the construction of special types of *boilers.* Now-a-days pressures of the order 15 to 30 atmospheres are generally employed, but in steam turbines pressures as high as 200 atmosphers have been used. The steam is generated in a boiler which is so designed that the hot gaseous products of combustion may remain as long as possible in contact with the surface of the boiler and thus deliver maximum heat to it. In the *furnace-tube boilers* generally employed in locomotives, the furnace gases pass through many separate tubes running throughout the boiler. In *water-tube boilers* the boiler itself consists of a system of tubes carrying water which are surrounded by the furnace flames. The steam leaving the boiler is often heated further (super-heated) without increase of pressure by allowing it to traverse again through tubes surrounded by furnace gases. This dry superheated steam then enters the cylinder.

If the exhaust steam from the cylinder is allowed to escape freely into the outer air as in the high-pressure or exhaust steam engine, it will have to overcome the atmospheric pressure and thus some work will be lost. To avoid this a *condenser* is used in the low pressure or condensing steam engine whose function is to produce a vacuum so that no work may be lost. Condensers in modern engines generally consist of a number of tubes carrying cold water which is kept in circulation by means of a pump, so that steam from the exhaust condenses on the surface of these tubes (*surface condenser*). The water and air produced by the condensing steam is removed by another pump.

If the steam were allowed to enter the cylinder all the time during a stroke, its pressure will always remain approximately equal to that in the boiler; thus in the backward stroke this high-pressure steam will be thrown to the exhaust and wasted. To prevent this, the steam inlet is closed before the piston has completed the stroke, the steam in the cylinder thereby expands and some extra work is obtained in this expansion. In order to obtain the maximum possible work from the steam, this expansion must be carried down to the pressure in the condenser. This would however require an impracticably long cylinder and consequently in *compound engines* this expansion is carried out in two or more cylinders. In the first cylinder the steam pressure falls to an intermediate value, and this exhaust steam from the first cylinder enters the second cylinder and so on, it being arranged that the pistons of all the cylinders assist one another in their motion either by being mounted on the same piston rod or through connection to a common shaft.

4·3. Efficiency of Engines.—The efficiency of any heat-engine is obtained from the first law of thermodynamics. A heat engine is merely an apparatus for the conversion of heat to work. The heat supplied is obtained by finding out the calorific value of the fuel consumed by burning a sample of the fuel in a bomb calorimeter (p. 106). If Q be the calorific value of the fuel consumed per unit of time, and W the power developed, we can define the *economic efficiency* of the engine as the ratio W/JQ. In the best steam engines about ½ kg. of coal is required per horse-power hour. This yields for the economic efficiency a value of 16 per cent.[1] The economic efficiency of smaller engines is much lower and may be as low as 3 per cent. This low value is partly due to heat losses caused by friction, radiation, etc. But it is clear that even if these could be eliminated completely the efficiency could not reach 100 per cent, an ideal which should be aimed at in perfect heat engines.

The question arises whether this lack of perfectness in heat engines is to be ascribed to their bad designing or whether there is something in the very nature of things which prevents us from converting the whole amount of heat to work.

This question was pondered over by Sadi Carnot over a hundred years ago. He showed that even with an ideal engine, it is never possible to convert more than a certain percentage of heat to work.

4·4. The Indicator Diagram.—It is very convenient to represent the behaviour of an engine by an indicator diagram and hence in discussing the theory and performance of heat engines this is always done. Suppose a certain amount of gas or liquid is contained in a vessel at a certain temperature and pressure and occupies a certain volume. The state of the substance is uniquely represented from the assignment of its pressure and volume. Thus we can represent the state of the gas by a point A (Fig. 2) on a graph such that the abscissa and the ordinate of A are the volume and the pressure of the gas respectively.

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[1] The calorific value of ½kg. of carbon when it is fully burnt is (See §5·16, eqn. 23) about $96 \times 500/12$ K cal. while one horse-power hour$=$652 K cal. Therefore efficiency $= 652/4000 = 16 \cdot 3\%$.

Let the pressure and volume of the gas be changed to that corresponding to the point B and suppose that the pressure and the volume throughout this change are represented by points on the line AB. Then this operation is represented by the line AB on the diagram. Such a trace is obtained in actual engines by means of a device called *indicator*, whose mode of action is as follows :—The backward and forward motion of the piston is communicated by the piston rod to the holder of a sheet of paper or a rotating drum and thus the movement of the paper (say in a horizontal direction) is a measure of the volume change. The pressure changes in the gas are recorded on the same paper by a pencil which is carried by another piston moving in another cylinder, this cylinder being attached to the main cylinder on one side and communicates with the latter. The pencil thus simultaneously records the pressure in the vertical direction and the piston displacement, *i.e.*, the volume in the horizontal direction. The resulting curve is called an *indicator diagram* or *p-V* diagram.

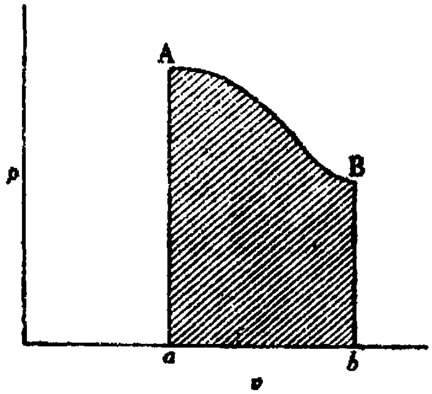

Fig. 2.—The indicator diagram.

As proved in Chap. II, the work done by a gas in expanding against a pressure p is pdv. For the finite process AB the work is $\int pdv$ = area A*ab*B. It is thus clear that the indicator diagram directly indicates the work done by the engine during each cycle of operations, the work being equal to the area enclosed by the indicator diagram. The work done is positive if the indicator diagram is traced in the clockwise direction and negative if the direction is anticlockwise. Indicator diagrams are therefore of great use in engineering practice.

The indicator diagram gives the work performed by the piston per stroke. Multiplying it by the number of strokes per second, *i.e.*, by twice the number of revolutions of the shaft we get the power indicated by the indicator which is generally expressed in horse-power—*indicated horse-power*. The power actually delivered by the engine is measured by a brake dynamometer and is called the *brake horse-power*, the ratio of this to the indicated horse-power being called the *mechanical efficiency* of the engine.

4·5. The Carnot Engine.—As we have seen, the function of the steam-engine is to convert the chemical energy stored in coal to energy of motion by utilising the expansive power of steam.

The machinery necessary for this purpose is however so complicated that one is apt to lose sight of the essential physical principles in the details of mechanical construction. Let us therefore discuss the physical principles involved in the running of a heat engine. Three factors are apparently necessary, *viz.*, a source of heat, a working substance, and suitable machinery. In the steam engine, the source of heat is the furnace where heat is supplied by the burning of coal. But we may get heat by a variety of other means, *e.g.*, by burning oil, wood, naphtha, or even directly from the sun (solar engines) or from the inside of volcanoes (as is sometimes done in Italy). We can therefore replace the furnace by the general term "*reservoir of heat*". For steam, we can use the general term "*working substance*," for any substance which expands on heating can be used for driving heat engines. As a matter of fact, we have got hot air engines in which air is heated by a gas burner or a kerosene lamp, and pushes the piston up and down as steam would do and is thus employed to do work. Mercury has also been used recently for this purpose.

In addition to the three requisites mentioned above, we require a fourth one, *viz.*, *the possibility of having a temperature difference*. This is at first not so apparent, but can easily be demonstrated. In a hot air engine the heated air can push the piston outward since the air outside is at a lower temperature. If there were no difference of temperature between the inside and the outside no difference of pressure could be created, hence the machine would not work. We therefore require not only a source of heat, but also a *Heat Sink*, *i.e.*, heat resevoir at a lower temperature. In steam engines, the surrounding air acts as the sink of heat or cold reservoir.

Carnot observed that the function of the heat-engine is to extract a certain quantity of heat Q from the heat reservoir F, convert a part of it to work and transfer the rest to the heat sink G. He also showed how these operations should be carried out so that the efficiency may be maximum.

Since whenever there is a difference of temperature, there is a possibility of converting heat to work, the converse is also true, *i.e.*, if we allow heat to pass from F to G by conduction, we miss our opportunity of getting work. Hence we must extract heat from F in such a way that loss of heat by conduction is reduced to a minimum. These considerations lead us to the following ideal arrangement.

F is a heat reservoir[1] at temperature T (Fig. 3), G a heat-sink at T'. S is the cylinder of the engine containing a perfect gas instead of steam as the working substance and fitted with a non-conducting piston. The walls of the cylinder are impervious to heat but the bottom is perfectly conducting. The behaviour of the working gas is shown by the indicator diagram showing the pressure and the volume of the gas at any instant. Let the following steps be performed :—

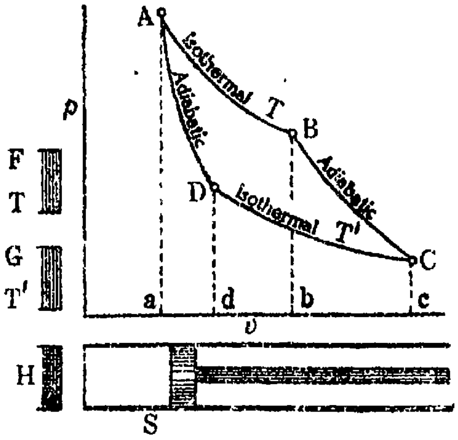

Fig. 3.—The ideal Carnot engine with indicator diagram.

(1) Let the initial temperature of the gas within S be T and let it be placed in contact with F, and the piston moved forward slowly. As the piston moves, the temperature tends to fall, and heat will pass from F to S. The operation is per-

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[1] For the purpose of argument both the hot and the cold reservoirs are assumed to be capable of absorbing or rejecting an unlimited supply of heat without suffering any appreciable change of temperature.

formed very slowly,[1] so that the temperature of the air is always T. The representative point on the indicator diagram moves from A to B, along an isothermal curve. The heat Q extracted in this process is equal to the work done by the gas in this expansion, and is given by

$$W_1 = Q = \int_A^B p\,dv = RT \log_e \frac{v_b}{v_a} = \text{area AabB}. \quad . \quad (1)$$

(2) F is then removed and H, which is simply a non-conducting cap, is applied to the cylinder, and the piston allowed to move forward by inertia. Then the gas will describe the adiabatic BC and will fall in temperature. We stop at C when the temperature has fallen to T'. The work done by the gas is given by

$$W_2 = \int_B^C p\,dv = \int_B^C \frac{K dv}{v^\gamma} = \frac{K}{1-\gamma}\left[\frac{1}{v_C^{\gamma-1}} - \frac{1}{v_B^{\gamma-1}}\right]$$

$$= \frac{1}{1-\gamma}\left[p_C v_C - p_B v_B\right] = \frac{R(T-T')}{\gamma-1} = \text{area BbcC}, \quad . \quad (2)$$

where $$pv^\gamma = K = p_C v_C{}^\gamma = p_B v_B{}^\gamma .$$

Since the pressure is now very much diminished, the gas has lost its expansive power, hence in order to enable it to recover its capacity for doing work it must be brought back to its original condition. To effect this we compress the gas in two stages: first isothermally along the path CD, and then adiabatically along DA. The point D is obtained by drawing the isothermal T' through C, and the adiabatic through A.

(3) During the isothermal compression, the cylinder is placed in contact with the sink G at T'. The heat which is developed owing to compression will now pass to the sink. This is equal to the work done on the gas and is equal to

$$W_3 = Q' = \int_D^C p\,dv = RT' \log_e \frac{v_c}{v_d} = \text{area CcdD}. \quad . \quad (3)$$

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[1] This is really a quasi-static process. In such a process the pressure and temperature of the enclosed gas are at all times infinitesimally near the corresponding quantities for the surroundings.

(4) The cylinder S is now placed in contact with H and the gas is compressed adiabatically. The work done on the gas by adiabatic compression is

$$W_4 = \int_A^D p\,dv = \frac{R}{\gamma-1}(T-T') = \text{area } DdaA. \quad . \quad . \quad (4)$$

It is thus seen that $W_2 = W_4$.

The net work done by the engine

$$W = W_1 + W_2 - W_3 - W_4 = \text{area ABCD} \quad . \quad . \quad . \quad (5)$$

$$= W_1 - W_3 = Q - Q' \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The last result can be written down directly from the first law of thermodynamics.

Since B and C lie on the same adiabatic, we have by equation (29) p. (83)

$$Tv_b^{\gamma-1} = T'v_c^{\gamma-1},$$

or

$$\frac{v_c}{v_b} = \left(\frac{T}{T'}\right)^{1/(\gamma-1)}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Similarly $\frac{v_d}{v_a} = \left(\frac{T}{T'}\right)^{1/(\gamma-1)} = \rho$, the adiabatic expansion ratio.

Hence

$$\frac{v_b}{v_c} = \frac{v_a}{v_d}.$$

Or

$$\frac{v_b}{v_a} = \frac{v_c}{v_d} = r, \text{ the isothermal expansion ratio.}$$

We have, therefore,

$$Q = RT \log_e r, \qquad Q' = RT' \log_e r,$$

and

$$W = Q - Q' = R(T-T') \log_e r. \quad . \quad . \quad . \quad (8)$$

Hence

$$\frac{Q}{T} = \frac{Q'}{T'} = \frac{W}{T-T'}. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

or

$$W = Q\left(\frac{T-T'}{T}\right). \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Thus the efficiency of the Carnot engine is

$$\eta = \frac{W}{Q} = \frac{T-T'}{T} = 1 - \frac{T'}{T} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$= 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Having analysed the mode of operation of the Carnot cycle, we now proceed to show that (1) it is reversible at each stage, (2) that no engine can be more efficient than the Carnot engine, (3) that the nature of the working substance is immaterial.

We may remark here that though in the foregoing we have considered a Carnot cycle with perfect gas as the working substance, yet the Carnot cycle can be performed equally well with a mixture of liquid and vapour as the working substance, only the calculation of efficiency will not be so simple and equation (12) will not be applicable. In fact Carnot cycle is merely a set of operations consisting of two isothermal and two adiabatic processes as explained above and can be performed by any thermodynamic system whatever, whether electrical, chemical, physical or magnetic.

4·6. Reversible and Irreversible Processes.—During any process performed on or with a system, its physical as well as chemical condition may change and this is generally associated with a change in the form of some of its energy content. If the system does not interact with the surroundings it is classed as a *closed* system, and its energy remains constant throughout. If the system returns to its initial state after undergoing through a series of operations it is said to perform a *cyclic process.*

All processes the effects of which can be completely annulled *everywhere* are called *reversible.* Hence even a cyclic process will not be reversible if it produces such changes in the surroundings which cannot be annulled by suitable methods. Thus for the process to be reversible, it must be performed in such a way that, at the end of the process, both the system and the surroundings may be fully restored to their initial states without producing any net change anywhere in the universe. It may be pointed out that these initial states are to be fully restored *in any manner* and by any means whatever. For reversibility it is not necessary that the annulling process should be identical with the direct process, differing from it only in being traced in the opposite direction. It is, however, evident that if the process can be traced in the opposite direction with all the thermal and mechanical effects remaining of the same magnitude but of opposite sign to that in the direct process, it will be reversible, as it can be completely annulled in this manner. If the whole system (including the surroundings) cannot be completely restored to its initial condition everywhere even with the use of all possible physical means, the process is said to be *irreversible.* It is not possible to specify forthwith some general experimental criterion to determine whether any suggested process will be reversible or not. A reference to the second law of thermodynamics (Chap. VI) is often necessary to determine whether a process is reversible or not. In fact it will be seen that it is a necessary consequence of the second law that *all natural processes are irreversible.* We shall now examine some typical processes and find out the conditions under which they will be reversible.

Consider first a purely mechanical process in which a perfectly elastic ball falls from some height upon a steel plate (supposed to be perfectly elastic). It is clear that no energy is dissipated in the process, the ball rises again to its initial height, and the process is reversible. Next suppose the plate is made of inelastic lead. The potential energy of the ball is transformed into its kinetic energy which causes deformation of lead producing heat through friction and this is irreversible since this heat cannot be reconverted by any means into the kinetic energy of the ball making it rise again to its initial height. Thus it will be seen that all purely mechanical processes in which friction and inelasticity are absent are reversible in every detail. Examples of these are the motion of perfectly rigid bodies and of incompressible fluids, the oscillation of a simple pendulum, the orbital motion of the planets, etc. provided of course friction is absent.

Another interesting case is the extension of a spring balance. When the spring is very slowly stretched work equal to $\int(F+\Delta F)dl$ is done upon it, F being the stress corresponding to the particular strain developed in the spring and ΔF the infinitesimal extra force necessary to bring about the process. If on the other hand the spring is allowed to contract slowly by the same amount, the spring does work equal to $\int(F-\Delta F)dl$ on the outside agency, and these two quantities of work differ from each other by an infinitesimal amount. Thus the stretching process can be completely annulled by the reverse process, the spring and the outside agency both being reduced infinitesimally near to their initial states and the process is reversible. It is however essential that the stretching must be produced or reduced gradually by the application of an external force which should differ infinitesimally at every instant from the stress developed in the spring, otherwise a part of the work will be spent in setting up vibrations of the spring and this will produce irreversibility. Such a process is called a *quasi-static* process and consists essentially of a succession of equilibrium states.

The case of elastic fluids is analogous to that of the spring. To every volume of the fluid in the equilibrium state there corresponds a definite stress or pressure, so that the amount of work done during the quasi-static processes of balanced expansion and balanced compression are almost exactly equal. It is important to note that the expansion should be balanced otherwise whirls and eddies (turbulent motion) will be set up in the fluid. This will produce irreversibility for two reasons :—(1) The work done by the gas cannot be determined from the expression $\int pdv$ as the parameter p is indeterminate, since on account of the finite velocity of the process and the consequent turbulence the fluid is not in a state of equilibrium. Due to this indeterminacy in the amount of work done the process is evidently irreversible. (2) The turbulent motion gradually subsides on account of dissipative forces like viscosity and friction with the production of heat. Thus in this process some work has been transformed through the mechanism of viscosity and friction into heat. In order to restore the system and the surroundings to their initial states this heat must be completely reconverted into work which is impossible from the second law (See §6·2, Kelvin-Planck statement). Such quasi-static or balanced expansions and compressions can be brought about easily by applying pressures on the piston enclosing the fluid and adjusting the pressure to differ from the fluid pressure by an infinitesimal amount.

It will be seen from the foregoing considerations that for reversibility a further condition is necessary, namely, that the substance should pass through equilibrium states only, *i.e.*, through states of mechanical and thermal equilibrium with the surroundings as well as internally. In other words, throughout the process the pressure and temperature throughout the working substance should be uniform (internal equilibrium) and differ only by an infinitesimal amount from the external pressure on the piston and the temperature of the reservoir respectively (external equilibrium). Such a process is called *mechanically reversible or quasi-static* and must, of necessity, be performed infinitely slowly[1] and can be performed just as well in one direction as in the other. For the process to be *thermodynamically reversible* it must in addition be not accompanied by any dissipative effects anywhere such as may arise from inelasticity, viscosity, friction, electrical resistance, magnetic hysterisis, etc. Thus a process is reversible[2] if it is (1) quasi-static and (2) non-dissipative.

It will be observed that it is impossible to satisfy perfectly the stringent conditions of reversibility. In fact a reversible process is purely an ideal abstraction, useful for theoretical calculations but we do not come across such processes in Nature just like the notions of point masses and weightless strings employed in mechanics.

For greater clarity we may add some more examples of reversible and irreversible processes. The transfer of heat from one body to another by conduction or radiation can be reversible only when the two bodies are at the same temperature or differ by an infinitesimal amount. If the two bodies have a *finite* difference of temperature the process of heat transfer is irreversible, since in order to annul the process we should be able to transfer the heat from the colder to the hotter body without producing changes anywhere in the universe which is impossible from the second law (see Clausius' statement §6·2).

Other examples of irreversible processes are Joule expansion (which is an example of unbalanced expansion or equalisation of pressure), Joule-Thomson expansion (Chap. XII), the condensation of a supersaturated vapour, the freezing of an undercooled liquid, all types of explosions, and all such processes in which friction, viscosity, electrical resistance in a conductor, magnetic hysterisis, inelastic deformations of a solid, mixing of two different substances, etc. play a part. In fact all spontaneous processes in Nature proceed at a finite speed and are therefore irreversible. Processes which are the result of a mere release such as the opening of a tap, the sapping of a wire when cut, bringing of two bodies in contact, etc. are also irreversible.

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[1] This artifice of infinitely slow velocity is very useful as it enables us to replace ordinary real processes in thermodynamical systems by conceptual reversible processes since several dissipative effects such as friction and viscosity tend to vanish at zero velocity.

[2] This yields a simpler definition of reversibility in case of mechanical processes as follows :—A mechanical process is reversible if the successive state of the process differ by infinitesimals from equilibrium states provided no dissipative effects are present anywhere.

Only reversible processes can be mathematically described in thermodynamics or represented by means of curves in diagrams since no unique values of temperature and pressure can be assigned to systems not in equilibrium.

The question might be pertinently asked : why are all naturally occurring processes in thermodynamics irreversible, particularly when in dynamical processes reversibility can be at least progressively attained as a limit by eliminating friction, inelasticity, etc. The answer was given by Boltzmann whose viewpoint, we shall take up in Chap. IX. He showed that irreversibility is confined to the behaviour of a complex structure like a gas treated as a whole and is not to be expected in the behaviour of the individual molecules, and arises from our inability to deal with the individual molecules. Further in the so-called irreversible process, reversibility is not impossible but is almost infinitely improbable.

4·7. Reversibility of the Carnot Cycle.—It is important to notice that the Carnot cycle is reversible at each stage, *i.e.*, instead of abstracting an amount of heat Q from a source at $T°$ and transferring a part Q' to a sink at T' and converting the balance $Q-Q'$ to work we can proceed in such a way that the machine abstracts the heat Q' from the sink at T', then we perform the work W on the machine, and the heat Q is transferred to the source at $T°$. This is done by proceeding along the reverse route ADCBA, *i.e.*, first allowing the gas to expand adiabatically from A to D, then allowing it to expand isothermally from D to C in contact with the sink at T', the heat Q' being extracted in the process. Then we compress the gas adiabatically till we reach the point B (temperature T). Then S is placed in contact with the source, the gas is further compressed isothermally till we reach A, and the heat Q is transferred to the body at the higher temperature T. The machine, therefore, acts as a *Refrigerator*, *i.e.*, by performing the work W on it, we are depriving a colder body at T' of the heat Q'.

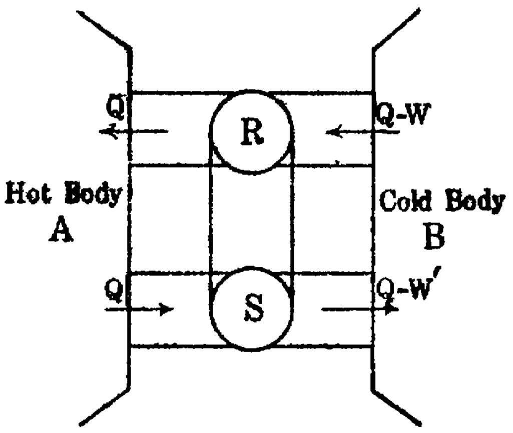
An engine in which the working substance performs a reversible cycle is called a *reversible engine*. Engines in which the cycle is irreversible are called *irreversible engines.* For the cycle to be reversible it is essential that the working substance should not differ sensibly in temperature from that of the hot body or the condenser when it is exchanging heat with them. There should be no transfer of heat by conduction in the usual sense, for it would be irreversible. This requires that the isothermal processes AB, CD should be described indefinitely slowly and the source and the condenser must have an indefinitely large capacity for heat so that their temperature, pressure and volume do not change appreciably during the process, and whatever change does take place, it takes place so very slowly that the reservoir always continues to be in a state of equilibrium and dissipative forces do not develop, *i.e.*, the changes in the reservoirs are quasi-static and non-dissipative.

Again the piston should move very slowly without friction. The changes in volume should be brought about quasi-statically by very small changes in the load on the piston in both the isothermal and adiabatic processes, so that the difference between the external pressure and the pressure of the gas should always be infinitesimal. Thus the Carnot cycle postulates a succession of stationary states of equilibrium while in an actual process the physical state is always changing. Further there should be no loss of heat by conduction from the gas to the piston and cylinder. It will thus be seen that the Carnot cycle with its perfect reversibility is only ideal and cannot be realised in practice.

Nevertheless it should be noted that for theoretical purposes the deviations from the ideal state may be rightly neglected if they are not an essential feature of the process and if they can be diminished as much as may be desired by suitable devices and then corrected for.

4·8. Carnot's Theorem.—The idea of reversibility is of the greatest importance in thermodynamics for the reason, that, working between the same initial and final temperatures *no engine can be more efficient than a reversible engine.* We now proceed to prove this important theorem with the help of the second law of thermodynamics.

Suppose[1] we have two engines R and S, of which R is a *reversible* engine and S an *irreversible* engine, and if possible, let S be more efficient than R. Suppose S absorbs the heat Q from A, converts a part W' to work and returns the rest, *viz.*, $Q-W'$ to the condenser. Let S be coupled to R (Fig. 4) and be used to drive R backwards. We are using R as a Carnot refrigerator.. By adjusting the quantity of the working substance it can be arranged that the engine R abstracts a certain amount of heat from B, has the work W performed on it, and returns the same heat Q to the source A. The amount of heat that R abstracts from B must equal $Q-W$. Now since S is assumed to be more efficient than R, $W'/Q > W/Q$, or $W' > W$ and hence $Q-W > Q-W'$, *viz.* R abstracts more heat from B than S restores to it. Thus the net result is that the compound engine RS abstracts heat $(Q-W)-(Q-W') = (W'-W)$ per cycle from B and converts the whole of it to work, while the source is unaffected. We are thus enabled, by a set of machines, to deprive a body continuously of its heat-content and convert the whole of it to work without producing any change in other bodies. The machine would thus work simultaneously as a motor and a refrigerator and would be the most advantageous in the world. It does not violate the first law for we are getting energy (work) out of the heat of the body B.



[2]Fig. 4.—Coupling a reversible and an irreversible engine.

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[1] If the two engines were to do the same work W while S absorbs the heat Q' from the source A and R returned the heat Q to A, the device of Fig. 4 would give us a self-acting machine which would continually transfer heat $Q-Q'$ from the condenser to the source without producing any changes elsewhere. This is impossible from Clausius' statement of the second law.

[2] Reproduced from Ewing's Steam Engine by the kind permission of Messrs Macmillan & Co.

Impossibility of Perpetual Motion of the Second Kind.—But still the process is quite as good as perpetual motion[1] of the first kind, for heat is available to us in unlimited amount in the atmosphere, in the soil or the ocean, and if the process were feasible we could run a power plant by using the heat of the atmosphere or drive a steamship by using the heat of the ocean. It would thus give all the essential advantages of a perpetual motion machine, *viz.*, that of getting work without any expense, though not without energy as a perpetual motion machine of the first kind was expected to do. Human experience[2] forbids us to accept such a conclusion. Hence the assumption which leads us to this wrong result must be incorrect. In other words *the irreversible engine cannot be more efficient than the reversible engine.*

Now consider two reversible engines R_1 and R_2 and let R_1 drive R_2 backwards in the manner shown in Fig. 4. If R_1 is assumed to be more efficient than R_2 we arrive, as before, at a result contrary to the second law. Hence R_1 cannot be more efficient than R_2. Similarly by making R_2 drive R_1 backwards we can show that R_2 cannot be more efficient than R_1. Therefore the efficiencies of R_1 and R_2 must be equal. Hence the *efficiency of all reversible engines is the same and this is the highest limit for the efficiency of any engine that can be constructed or imagined.* This is Carnot's theorem. Thus reversibility is the criterion of perfection in a heat-engine. Hence we see that the efficiency of a reversible engine is maximum and is independent of the nature of the working substances, being always equal to $1-T_2/T_1$, T_2 being the temperature of the 'sink' of heat and T_1 that of the source. We chose perfect gas as our working substance in §4·5, since its equation of state being known, we can easily evaluate η.

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[1] This was a term in use amongst the medieval philosophers who thought that a machine might be invented some day which will create work out of nothing. For some mechanical contrivances which were intended to produce perpetual motion, see Andrade, *Engines*, page 14. The gradual evolution of the Law of Conservation of Energy leading to the first law of thermodynamics showed that the idea is purely chimerical, since energy can never be created out of nothing, but can only be transformed from one form to another. The continual working of a machine that would create its own energy in violation of the first law of thermodynamics is called 'perpetual motion of the first kind'. The continual operation of a machine which would work by utilising the energy of only one reservoir in violation of the second law is called '*perpetual motion of the second kind*'.

[2] This result of human experience constitutes the second law of thermodynamics which has been stated in various equivalent forms. Kelvin stated the second law in the form :—It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects. Kelvin's statement is directly applicable to the present case. For fuller discussion, see Chap. VI.

NOTE:—It may be mentioned that Carnot was ignorant of the true nature of heat at the time (1824) when he published his theorem of efficiency. He followed the old caloric theory in his speculations which we know is wrong. Later it was shown by Clapeyron that Carnot's results remained intact when the Kinetic Theory of heat was introduced.

Exercise. 1. Discuss the irreversibility of the following phenomena:—Stirring of a viscous liquid, flow of electricity through a resistor, a compressed spring dissolving in acid, a waterfall, lightning, spontaneous combustion of phosphorus, tearing of paper.

2. What is the efficiency of a Carnot engine working between the temperature 300°C and 15°C? If 1000 calories of heat are absorbed by the engine at the higher temperature calculate the work done by the engine.

4·9. Theory of the Steam Engine. Carnot's Cycle with Steam.—Fluids are commonly used as the working substance in heat engines. In the steam engine, as we saw in the foregoing pages, the working substance is a mixture of water and water vapour. To calculate the performance of such an engine theoretically we shall first imagine an ideal steam engine performing Carnot's cycle. The various operations can be performed with the particular cylinder of §4·5 in the following manner:—

Starting from the point A (Fig. 5) let the piston be moved outwards and the substance expand isothermally at pressure p_1 and temperature T_1 taking in heat from the source. p_1 is the pressure which saturated steam would exert at the temperature T_1. This part corresponds to the conversion of water into steam and is represented by AB in Fig. 5. Next let the steam expand

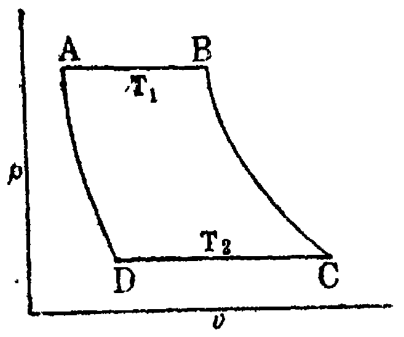

Fig. 5.—Carnot cycle with steam as working substance.

adiabatically doing work on the piston till its temperature falls to T_2, the temperature of the condenser. This is represented by BC. In the third stage compress the substance isothermally at the saturated vapour pressure p_2 of steam till the point D is reached such that an adiabatic compression completes the cycle and takes us to the point A.

The cycle is completely reversible and hence the efficiency of the engine is, from Carnot's theorem, $(T_1 - T_2)/T_1$. This cycle, however, has been performed with the working substance always in the same cylinder. But we know that with a view to prevent the wastage of heat consequent on alternate heating and cooling of the cylinder, modern steam engines are provided with separate boiler, cylinder and condenser. Still, however, if the working substance were to perform the same cycle the efficiency would be the same even if parts of the cycle are performed in different vessels. But with the organs so separated the adiabatic compression of the working substance from T_2 to T_1 in the last stage of the cycle becomes impracticable. We have consequently to heat it externally from T_2 to T_1. Hence the standard with which the performance of an actual steam engine may be compared is not the Carnot's cycle, but Rankine's cycle which is described in the next section.

4·10. Rankine's Cycle.—In Rankine's cycle the processes (*i*) and (*ii*) are the same as above but operation (*iii*) is continued till all the steam is condensed at the pressure p_2 and temperature T_2. Then by means of a separate feed-pump the condensed water is transferred to the boiler and the pressure is thereby increased from p_2 to p_1. In the boiler the water is heated to T_1 and then it reaches the initial state to begin the cycle afresh. It must be emphasized that all processes in the Rankine cycle are assumed to be performed reversibly so that no complications arise due to possible irreversible heat transfers, friction and acceleration and turbulence produced by the rushing of steam from one part to another.

The cycle is represented in Fig. 6, p. 244 on a p-V diagram. AB corresponds to the conversion of water into steam in the boiler and its admission into the cylinder, BC the reversible adiabatic expansion in the cylinder, CD the transfer of wet steam from the cylinder to the condenser and its reversible isobaric isothermal condensation into saturated water and DA the transfer by the feed-pump to the boiler which is assumed to be a reversible adiabatic compression of water from p_2 to p_1. In this process there is practically no change of temperature. At A the water is first heated from the temperature T_2 to T_1 in the boiler and subsequently converted into steam. The process AB in the ideal case includes (1) the reversible isobaric heating of water to the boiling point, (2) the reversible isobaric isothermal vaporization of water into saturated steam, (3) any possible superheating brought about in a reversible isothermal and isobaric manner. The indicator diagram for an ideal engine performing Rankine's cycle is represented by ABCD. The work done by a steam engine following the ideal Rankine cycle will be thus equal to the area of the indicator diagram. This area can be calculated in much the same way as in §4·5 if we know the equation of state of steam. This process is very cumbrous and in engineering practice a very simple procedure is adopted.

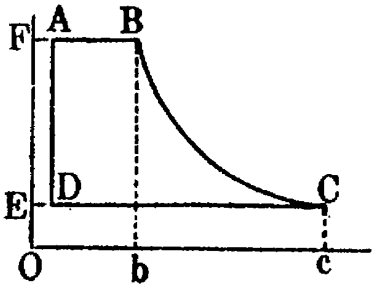

Fig. 6.—Rankine's cycle with steam.

Let us introduce the total heat function $H=U+pV$. Then

$$dH = dU+pdV+Vdp. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

From the first law of thermodynamics we have for any adiabatic process $dU+pdV=0$. Hence equation (13) yields for an adiabatic process

$$dH = Vdp. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Integrating between the limits B, C (Fig. 6) we get

$$H_B - H_C = \int_C^B Vdp. \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The right-hand side represents the area FBCE. On subtracting from it the area FADE we shall get the area ABCD which is the work done by the engine. The figure FADE approximates to a rectangle since the volumes represented by ED and FA may be taken to be equal (because the compressibility of water is small). Let this be equal to V_w per gram-molecule of water at p_2 or p_1 and T_2. Hence the area FADE is equal to $(p_1-p_2)V_w$, this expression being generally known as the feed-pump term. Therefore the work[1] done in Rankine's cycle per gram-molecule of steam is

$$H_B - H_C - (p_1 - p_2)V_w = H_B - H_C \text{ approx.}, \quad . \quad . \quad (16)$$

since the so-called feed-pump term is small and negligible. Thus the work done per gram-molecule of steam is measured by the heat-drop $H_B - H_C$. This will hold whether the steam is superheated, saturated or wet. The value of $H_B - H_C$ under adiabatic conditions can be easily found with the help of Mollier's diagrams as explained in §4·13.

The engine takes heat Q_1 during the process AB and rejects heat Q_2 during the process CD. Since the process AB is isobaric, the heat Q_1 taken by the engine is, from (13) and the first law, given by

$$Q_1 = \int (dU + pdV) = \int_A^B dH = H_B - H_A \quad . \quad . \quad . \quad (17)$$

Since H_A is not listed in the steam tables we have to express it in terms of H_D. Since the process DA is adiabatic we have from (14)

$$H_A - H_D = \int_D^A V\,dp = (p_1 - p_2)\,V_w, \quad . \quad . \quad (18)$$

since V can be treated as constant and equal to V_w. Hence the efficiency of the Rankine cycle is

$$\eta = \frac{H_B - H_C - (p_1 - p_2)V_w}{H_B - H_D - (p_1 - p_2)V_w} = \frac{H_B - H_C}{H_B - H_D} \text{ approx.}, \quad . \quad . \quad (19)$$

It will be seen that the efficiency in Rankine's cycle is less than in Carnot cycle for in the former some heat (*viz.*, that required to heat the feed-water in the boiler from T_2 to T_1) is taken at a lower temperature. This will be obvious from Fig. 8.

4·11. Entropy-Temperature Diagrams.[2]

—We have so far represented the Carnot and Rankine cycles on the usual indicator diagram in which the volume denotes the abscissa and the pressure denotes the ordinate. Another way to represent the cycle, which is often found very useful, is by plotting the temperature of the working substance as ordinate and the entropy as abscissa. Its importance is readily perceived for during any reversible expansion the increase dS in entropy is given by

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[1] This can be calculated in another way also. From the first law of thermodynamics the work done $= Q_1 - Q_2$ and $Q_1 = H_B - H_A$ from (17), $Q_2 = H_C - H_D$. Hence using (18) we get (16).

[2] §4·11—4·13 should be read after the reader becomes familiar with the quantity 'entropy' which is formally introduced in Chap. VI.

$$dS = \frac{dQ}{T}. \quad \therefore \quad \int T dS = \int dQ,$$

where the integration is performed between the limits of the expansion. Thus the area of the curve on the entropy-temperature diagram represents the amount of heat taken up by the substance.

We can now easily represent the Carnot and Rankine cycles on the entropy-temperature diagram. The Carnot cycle is represented in Fig. 7. AB represents the isothermal expansion at $T_1°$, BC the reversible adiabatic expansion, CD the isothermal compression at T_2, the temperature of the sink, and DA the final adiabatic compression. It is evident that lines AB and CD will be parallel to the entropy-axis and BC, AD will be parallel to the temperature-axis. The amount of heat taken in is represented by the area AB*ba*, heat rejected by the area DC*ba*, the difference ABCD being converted into work. It is readily seen that these areas are respectively equal to $T_1(S'-S)$, $T_2(S'-S)$ and $(T_1-T_2)(S'-S)$, and the efficiency is $1-T_2/T_1$.

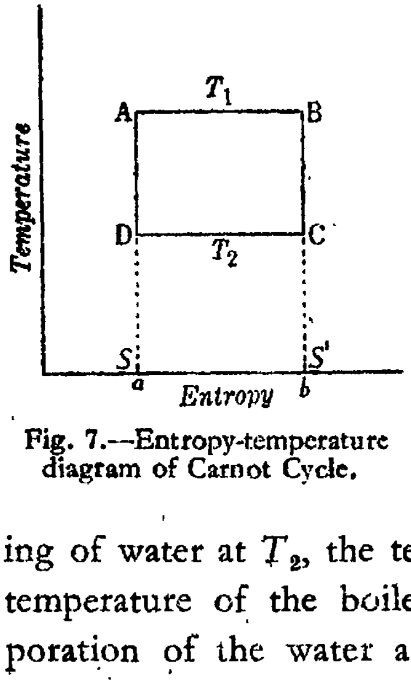

Fig. 7.—Entropy-temperature diagram of Carnot Cycle.

The Rankine cycle is represented in Fig. 8. DA represents the heating of water at T_2, the temperature of the condenser, to T_1 the temperature of the boiler, AB the evaporation of the water at T_1 into steam at T_1, BC the adiabatic expansion of steam down to the temperature of the condenser, CD the isothermal compression in the condenser when it becomes liquefied. The total heat taken in by the working substance is represented by the area DAB*bd*D, the heat rejected by the area C*bd*D and hence the work done is represented by the area ABCD. The efficiency of the engine will be equal to area ABCD ÷ area AB*bd*DA, and it is

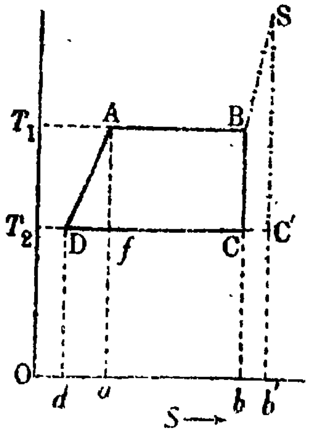

Fig. 8.—Entropy-temperature diagram of Rankine Cycle.

evident from the diagram that it will be less than that for a Carnot engine working between the same temperatures which is equal to area ABC*f* ÷ area AB*ba*, though of course the amount of work obtained is greater than the work in a Carnot cycle. Clearly the decrease in efficiency is due to the fact that the heat represented by the area DA*ad* is taken not at the highest temperature T_1 but at somewhat lower temperature.

In actual practice superheated steam is employed. The superheating is represented by the line BS in which the substance takes in an additional quantity of heat represented by the area BSC′*b*′*b*. The cycle with superheated steam is represented by the curve DABSC′D. It is readily seen that the efficiency is increased by superheating, because some heat is taken at a higher temperature though the advantage gained is not very great.

4·12. Entropy of Steam.—For plotting the above entropy-temperature diagram we must know the entropy of steam under different conditions. Assuming the entropy of water at 0°C. ($T_0 = 273\cdot2$) and under its own saturation pressure to be s_0, the entropy of steam (assumed to be wet) per gram at any temperature T_1 will be given by

$$s_1 = \int_{T_0}^{T_1} \frac{\sigma dT}{T} + \frac{qL_1}{T_1} + s_0,$$

where σ is the specific heat of water at constant pressure, T_1 the boiling point of water, L_1 the latent heat at $T_1°$ and q denotes the dryness of steam, *i.e.*, q is the proportion of dry steam in the mixture expressed as a fraction of the whole[1]. Assuming σ to be constant

$$s_1 = \sigma \log_e T_1 - \sigma \log_e T_0 + \frac{qL_1}{T_1} + s_0 \qquad . \quad . \quad (20)$$

If the steam is superheated to $T_2°$ an extra factor $\int_{T_1}^{T_2} c \frac{dT}{T}$ should be added on the right-hand side, c denoting the specific heat of steam during superheating. s_0 the entropy of water at $T_0°$ (0°C) and under its own saturation pressure is usually taken to be zero. In this way the entropy of steam in any given state can be calculated and the ideal performance expected of an engine can be found from Fig. 8. Such values have been calculated and are given in Steam Tables[1] and thus the work obtainable from an engine can be easily calculated. In engineering practice however it is found more convenient to calculate it graphically with the help of Mollier's diagrams.

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[1] In writing out the above expression for entropy we have omitted the term arising from the increase of saturation pressure. This is so small that for practical purposes it can be neglected.

4·13. Mollier's Diagrams.—We have seen in §4·10 that the work obtainable per gram of steam in going through the Rankine cycle is given by the heat drop $h_B - h_C$ during reversible adiabatic expansion and the efficiency by $(h_B - h_C)/(h_B - h_D)$. To be able to calculate these quantities we must know the value of the total heat h of steam under different conditions of temperature and pressure. For engineering work this has been calculated for different states of steam and is given in steam tables. It is however found more convenient to represent these graphically. Such diagrams were first introduced by R. Mollier in 1904 and can now be had in the market.

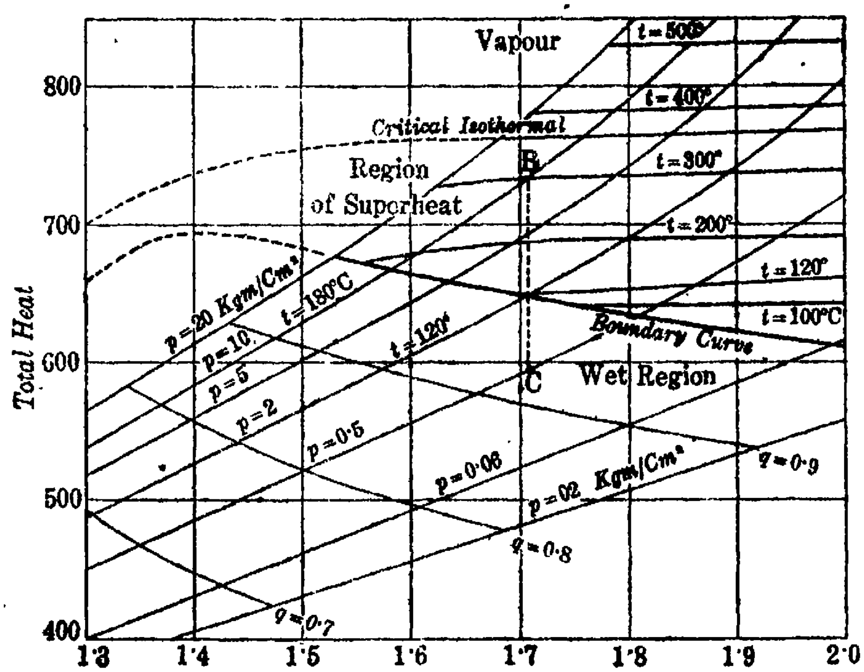

Fig. 9.—Mollier diagram for steam.

A portion of the Mollier diagram of total heat and entropy is represented in Fig. 9 on a small scale and in skeleton form.[2] The boundary curve separates the heterogeneous mixture of water and saturated steam (wet region) from dry superheated steam (region of superheat) on the top and from water on the extreme left bottom (not shown). Above the critical isothermal there is vapour or gas only. Further the critical point K lies on the boundary curve which thus touches the critical isothermal at K. To the left of K between the boundary curve and the critical isothermal there is the liquid state (water) only. The vertical lines, being lines of constant entropy, represent the adiabatics (isentropics). Lines of constant pressure are drawn throughout the chart extending from the wet region, where they are straight and coincide with the isothermals, across the boundary to the region of superheat where they become curved. The slope of the constant pressure lines is given by $(\partial h/\partial s)_p = T$ since $dh = Tds + vdp$. This is why in the wet region the slope of the isobaric lines is constant and equal to the absolute temperature. The pressure p is expressed in kilograms per sq. cm. In the wet region there are also lines of constant dryness for different values of q. In the region of superheat there is a system of lines of constant temperature which on crossing the boundary curve coincide with the lines of constant pressure in the wet region. Similarly there are isothermal and isobaric lines in the regions of liquid and vapour also.

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[1] For the details of calculation of entropy and total heat of steam in different states see Callendar, *Properties of Steam* (Arnold); or Ewing, *The Steam Engine and other Heat Engines*, Chap. III.

[2] Actually big charts are available from which the total heat corresponding to any state of steam can be accurately read.

The method of using the diagram is very simple. Suppose the steam enters the cylinder at a pressure of 10 kg. per sq. cm. and temperature 300°C. This state is represented by B in the Mollier diagram, and h_B corresponding to this can be easily read. The adiabatic expansion will be represented by a vertical line in the diagram. Thus if the condenser pressure is 0·5 kg./sq. cm. this expansion will be represented by the dotted line BC where C lies on the line $p = 0{\cdot}5$. The value of h_C corresponding to the state C can be read. Thus the heat-drop $h_B - h_C$ is known. The state of dryness of steam can also be read if desired. Similarly the other quantities occurring in equation (19) can be found.

4·14. Performance of Actual Steam Engines.—Various causes combine to make the efficiency of an actual engine fall below the Rankine ideal. In the piston and cylinder type of engine, the main causes of this are the incomplete adiabatic expansion before release and conduction of heat from the steam through the cylinder and piston. Complete expansion would require a large cylinder with its accompanying disadvantages.

An actual indicator diagram for a steam-engine is shown by continuous lines in Fig. 10. The corresponding Rankine cycle is represented by ABCD. It will be seen that the toe of the ideal cycle is cut off. For a complete explanation see Ewing, *The Steam Engine and Other Heat Engines*, Chap. III. The efficiency in ordinary engines is only 60 per cent of the Rankine ideal and in rare cases reaches 70 per cent. This ratio is called the ***efficiency ratio.*** This of course refers only to the fraction of heat energy of steam converted into work. To find the rate of fuel consumption we must know the heat loss in furnace boiler, etc.

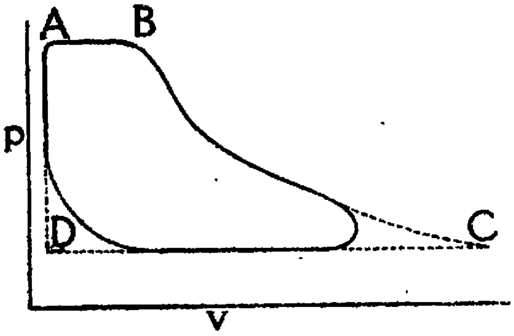

Fig. 10.—Actual indicator diagram for a steam engine.

Problems 1. Find the increase in entropy when 10 grams of ice at 0°C. melt and produce water at the same temperature, given that the latent heat of fusion of ice = 80 calories/gm.

2. Find the entropy of saturated steam at a pressure of 74 lbs. per sq. in.

[From the tables the boiling point at this pressure is 152·6°C, and the latent heat at this temperature is 503·6 cal./gm. The entropy of 1 gm. of water at 152·6°C or 425·6°K is $1 \times \log_e (425 \cdot 6/273) = 0 \cdot 44$ cal./deg. The increase in entropy due to evaporation at 425·6°K is $503 \cdot 6/425 \cdot 6 = 1 \cdot 18$ cal./deg. Therefore the entropy of one gram of steam at 425·6° K is $\cdot 44 + 1 \cdot 18 = 1 \cdot 62$ cal./deg., assuming the standard zero state of water to be at 0°C. under its own vapour pressure.]

3. Calculate the efficiency of an engine performing a Rankine cycle with a boiler pressure of 10 kg./cm.^{2} and a boiler temperature of 300°C., the temperature of the condenser being 36°C.

[From tables the vapour pressure at 36°C. is about 0·06 kg./cm.^{2} and the total heat of water under saturation pressure at this temperature is 35·9 cal./gm. From Fig. 9 the adiabatic expansion takes place from B along BC upto the point of intersection with curve $p = \cdot 06$. Hence $h_B = 733$ and h_C for the intersection point with $p = \cdot 06$ is 525. Hence

$$\text{efficiency} = \frac{733-525}{733-35 \cdot 9} = 0 \cdot 30 = 30 \text{ per cent.}$$

In actual engines the efficiency is much lower on account of irreversible processes.]

INTERNAL COMBUSTION ENGINES

By the term 'internal combustion engine' is meant a type in which no separate furnace is used but heat is generated inside the cylinder itself.[1]

4·15. Historical Introduction.—Like other types of heat engines, the idea of this type also dates from medieval times. Ch. Huygens, the great Dutch physicist, proposed in 1680 the construction of an engine consisting of a vertical cylinder and piston, in which the piston would be thrown upwards by the explosion of a charge of gunpowder. This would fill the cylinder with hot gases which would eventually cool, and the piston would be forced down by gravity. Each stroke would require a fresh charge of gunpowder.

This engine was never realised, probably owing to the difficulty of introducing fuel after every explosion but the idea persisted. The discovery of combustible gases (coal gas, producer gas....) and of mineral oils brought the idea within the range of practical possibility, as the difficulty of supplying fuel promised solution. But many long years of practical and theoretical study were necessary before such engines became commercially possible.

It is not possible to go into the details of these early attempts, and it will suffice to describe and explain the action of the two types[2] which have ultimately survived, *viz.*, (1) the Otto engine in which heat is absorbed at *constant volume*, (2) the Diesel engine in which heat is absorbed at *constant pressure*. Nearly 80 per cent of internal combustion engines today are of the Otto type. We shall compare the action of these engines with that of the ideal Carnot engine in which heat is absorbed at *constant temperature*. But we may mention, in passing, the historical Lenoir engine (1860) which is a direct ancestor of the Otto engine. In this, a mixture of gas and air was sucked into the cylinder by the forward motion of the piston, and while the piston was half-way along the cylinder, the mixture was ignited by an electric spark and the piston was driven out and completed the stroke. Then by the backward stroke of the piston the gaseous mixture was forced out and a fresh charge was again sucked in for the next cycle.

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[1] These may be contrasted with the steam engine which may be called *external* combustion engine because heat is produced in the boiler. The internal combustion engine is much more efficient than the steam engine because the working substance can be heated to a much higher temperature (2000°C).

[2] Sometimes internal combustion engines are divided into (1) gas engines, (2) oil and petrol engines. It is however more scientific to divide them with regard to the cycles they follow and not with regard to fuel. Hence the engines have been divided into the constant volume, constant pressure and constant temperature type.

The Lenoir engine was not a success owing to the large amount of fuel which it required, but it has been the forerunner of more modern types of engines.

4·16. The Otto Cycle.—The Otto cycle which we are now going to describe was originally proposed by Beau de Rochas (1862), but the practical difficulties were first overcome by Otto in 1876. The working of the engine will be clear from Fig. 11. The engine consists of the cylinder and the piston, the cylinder being provided with inlet valves for air and gas (if gas is used for combustion), and exhaust valves. The opening and closing of these valves are controlled by the motion of the piston. There are four strokes in a complete cycle :—

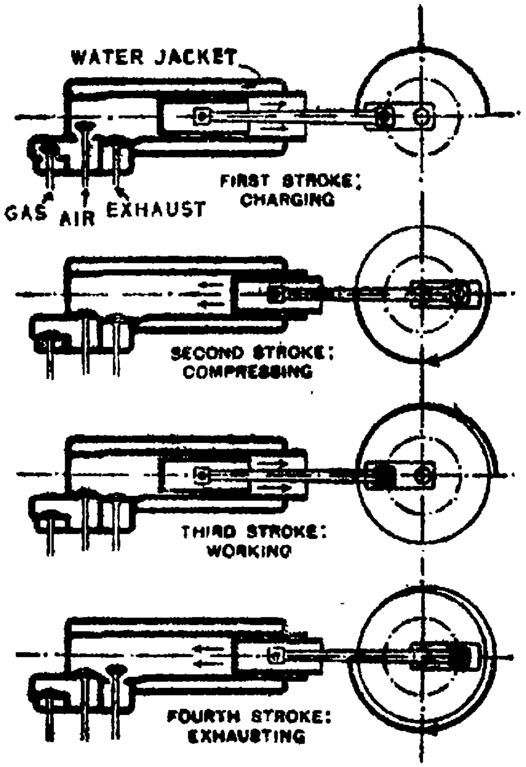

Fig. 11.—The four strokes of the Otto engine.

(*i*) *The Charging Stroke.*—In this the inlet valves are open and a suitable mixture of air and gas is sucked into the cylinder by the forward motion of the piston.

(*ii*) *The Compression Stroke.*—During this stroke all the valves are closed, and the combustible mixture is compressed adiabatically to about 1/5th of its original volume by the backward motion of the piston. The temperature of the mixture is thereby raised to about 600°C.

At the end of the compression stroke, the mixture is fired by a series of sparks.

(*iii*) *The Working Stroke*.—The piston is now thrown forward with great force, since owing to combustion a large amount of heat is developed which raises the temperature of the gas to about 2000°C. and a correspondingly high pressure is developed.

(*iv*) *The Scavenging or the Exhaust Stroke*.—At the end of the third stroke, the cylinder is filled with a mixture of gases which is useless for further work. The exhaust valves are then opened, and the piston moves backward and forces the mixture out. After scavenging is complete, a fresh charge of gas and air is sucked in and a fresh cycle begins.

For purposes of theoretical discussion we assume the cycle to be performed under certain ideal, conditions, *viz.*,(1) all processes are quasistatic, so that there is no acceleration, (2) there is no friction and no loss of heat by conduction through the walls of the cylinder. The thermodynamical behaviour is illustrated in the indicator diagram of Fig. 12.

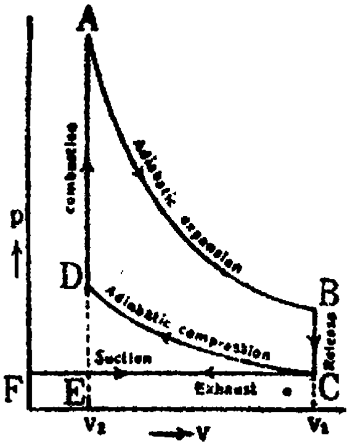

Fig. 12.—Four-stroke Otto cycle.

It should be remembered that air is the working substance in the Otto engine, the function of gas or petrol being merely to heat the air by its combustion. EC represents the isobaric suction stroke (gas and air being sucked in at atmospheric pressure). CD represents the adiabatic compression stroke. At D (pressure about 5 atmospheres, temperature about 600°C.) the mixture is fired by a spark. A large amount of heat is liberated, and the representative point shifts to A (temperature 2000°C. pressure about 15 atmospheres), volume remaining constant. We assume the process to take place in a quasistatic isochoric manner. AB represents the working stroke which indicates a quasistatic adiabatic expansion of the gas. At B the exhaust valve is opened, and the pressure falls to the atmospheric pressure CV_1. We assume this process also to take place in a quasistatic isochoric manner. CE is the isobaric scavenging or exhaust stroke.

The *efficiency* of the engine can be very easily worked out. The processes EC and CE cancel each other and need not be considered any further. The exchange of heat takes place only during the processes DA and BC. The amount of heat taken during the process DA is equal to $C_v(T_a-T_d)$, where C_v is the specific heat at constant volume. (We suppose that this quantity retains the same value between 600°C. and 2000°C., which is only approximately true). Similarly heat rejected during BC is $C_v\,(T_b-T_e)$. Hence efficiency

$$\eta = 1 - \frac{T-_bT_e}{T_a-T_d}\,.$$

From the relation $TV^{\gamma-1}$ = constant for an adiabatic (see p. 83 equation 29), we obtain

$$\frac{T_a}{T_b} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \frac{T_d}{T_e} = \rho^{\gamma-1}, \qquad . \quad . \quad . \ (21)$$

where ρ is the adiabatic expansion ratio. Hence

$$\frac{T_b-T_e}{T_a-T_d} = \left(\frac{1}{\rho}\right)^{\gamma-1}.$$

Therefore the efficiency

$$\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \qquad . \quad . \quad . \ (22)$$

Taking $\rho = 5$, $\gamma = 1{\cdot}4$ we get

$$\eta = 1 - \left(\frac{1}{5}\right)^{0\cdot4} = 0\cdot52 = 52 \text{ per cent.}$$

The efficiency is generally much less due to turbulence, acceleration, thermal conduction, etc. which are usually present.

It will be seen that the expression obtained here for the efficiency in terms of the adiabatic expansion ratio is similar to that for a Carnot cycle (see equation 12 p. 233). The question arises : why not try to make the Carnot cycle a practical possibility ?

We shall now treat this question in more detail. In designing a machine, other factors have to be taken into consideration besides the mere question of theoretical efficiency. The engine must be, in the first place, quick-acting, *i.e.*, a cycle ought to be completed as quickly as possible. This practically rules out the Carnot engine as it takes heat at constant temperature, the process is therefore very slow and the engine becomes very bulky and heavy in relation to the power output. In the Otto engine the absorption of heat is almost instantaneous. But even where quickness is not the deciding factor, there are other weighty arguments against the adoption of the Carnot cycle. Pressure inside the cylinder varies during a cycle, and the machine must be so designed that it can withstand the maximum pressure. At the same time, we must obtain a reasonable amount of work per cycle.

4·17. To bring out the point clearly, we introduce a new quantity —"Mean effective pressure". As the name indicates, it is a measure of the mean pressure to which the cylinder is subjected during the cycle, and is therefore equal to the total work obtained during a cycle divided by the maximum amplitude of volume change. For the Carnot cycle (see Fig. 3, p. 231)

$$p_m = \frac{\text{Area ABCD}}{V_c - V_a},$$

and the maximum pressure is p_a.

We have now to calculate p_m for the different engines and find out the ratio p_a/p_m.

Carnot Cycle.—In the Carnot cycle, as well as in the Otto, p_c and T_c are fixed (atmospheric pressure and temperature). The comparison should be carried out for equal maximum temperature T_a. Let us assume $T_a = 2040°\text{K}$, and $T_c = 340°\text{K}$. We have therefore C fixed in the indicator diagram (Fig. 3). We draw the isothermal CD and the adiabatic CB through C. B is fixed by the final temperature chosen, *viz.*, 2040°K. We then draw an isothermal through B. A may be taken anywhere on this curve. We have therefore to take the isothermal expansion ratio $r = V_b/V_a = V_c/V_d$ as our independent variable.

The adiabatic expansion ratio

$$\rho = \frac{V_c}{V_b} = \frac{V_d}{V_a} = \left(\frac{T_a}{T_d}\right)^{\frac{1}{\gamma-1}} = x^{\frac{1}{\gamma-1}} \text{ (say)}, \quad . \quad . \quad (23)$$

where $x = T_a/T_c$ and is therefore fixed. We have to express every quantity in terms of the unknown r and the known ρ, T_c, p_c, T_a.

It can now be proved that

$$p_a \text{ (maximum pressure)} = p_c\, r\, \rho^{\gamma} = p_c\, r\, x^{\gamma/(\gamma-1)} \quad . \quad . \quad . \quad (24)$$

$$V_a \text{ (minimum volume)} = V_c/r\rho.$$

$$\text{Work available} = \text{R}\,(T_a - T_c)\log_e r.$$

$$\therefore\ p_m = \frac{\text{Work}}{V_a - V_c} = \frac{[(T_d/T_c)-1]\log_e r}{1-(1/r\rho)}\, p_c.$$

We have $$x = T_a/T_c = 6.$$

Hence $$\rho = \left(\frac{T_a}{T_c}\right)^{1/(\gamma-1)} = 6^{2\cdot56} = 98\cdot2,$$

if we put $\gamma = 1\cdot39$ for air.

The adiabatic expansion ratio thus reaches the enormous value of 98·2. If r is chosen to be 2 we get $V_c/V_a = 196\cdot4$.

The maximum pressure from (24) is given by $p_a = 2\times 98\cdot 2\times 6 =$ 1178 atmos., $p_m = (6-1)\log_e 2 = 3\cdot 47$ atmos.

$$\therefore \quad \frac{p_a}{p_m} = \frac{1178}{3\cdot 47} = 339.$$

$$\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} = 1 - \frac{T_c}{T_a} = 83 \text{ per cent.} \qquad (25)$$

These figures show that the Carnot engine must be designed to withstand a pressure of 1178 atmospheres, and should have an expansion ratio of 196. It has to be very bulky and very stout. The power output is too small compared to its bulkiness and stoutness.

The Otto Cycle.—Let us now calculate the same quantities for an Otto engine.

In this case, we take the same values for p_c, T_c and T_a. C is therefore fixed on the indicator diagram (Fig. 12). We draw the adiabatic CD and the isochore CB. D can be taken arbitrarily on CD, but the temperature should not exceed a certain value, which is determined by the ignition point of the mixture, otherwise the mixture will fire before the spark is allowed to pass. T_d should be about 600°K; we choose 612° K for convenience of calculation. The adiabatic expansion ratio ρ is therefore fixed. We have from (23)

$$\rho = \left(\frac{612}{340}\right)^{1/(\gamma-1)} = 4\cdot 5 \quad \text{(nearly).}$$

The adiabatic expansion ratio ρ is now enormously diminished.

Efficiency $\qquad \eta = 1 - \left(\dfrac{1}{\rho}\right)^{\gamma-1} = 44\,\%$

The ratio $\qquad \dfrac{T_a}{T_d} = x = \dfrac{10}{3} = \dfrac{T_b}{T_c}.$

It can now be easily shown that

$$p_a = x\rho^{\gamma}\, p_c = \text{about 27 atmospheres.}$$

Work obtainable from each cycle

$$W = C_v\,(T_a - T_d) - C_v(T_b - T_c) = C_v\,(x-1)\,(T_d - T_c)$$

$$= C_v\,T_c\,(x-1)\left(\frac{T_d}{T_c} - 1\right) = \frac{5}{2}\,p_cV_c\;(x-1)\left(\frac{T_d}{T_c} - 1\right)$$

and

$$V_a = V_c/\rho.$$

$$\therefore \text{ Amplitude of stroke} = V_c\left(1 - \frac{1}{\rho}\right).$$

$$p_m = \frac{5}{2}\,p_c\,(x-1)\left(\frac{T_d}{T_c} - 1\right)\Big/\left(1 - \frac{1}{\rho}\right) = 6 \text{ atmos.}$$

$$\therefore \quad \frac{p_a}{p_m} = 4\cdot 5.$$

The Otto cycle, therefore, fulfils all the conditions of practical possibility though the efficiency is rather low.

4·18. The Diesel Cycle.—Diesel was dissatisfied with the low efficiency of the Otto engine and began investigations with the idea that the efficiency of the Carnot cycle may be reached by certain other contrivances. He did not succeed in his attempt, but was led to the invention of another engine which, for certain purposes, presents some advantages over the Otto engine.

The great superiority of the Otto engine over the earlier Lenoir engine was in the use of the compression stroke before ignition. Since $\eta = 1-(1/\rho)^{\gamma-1}$, it is easily seen that if the compression ratio ρ can be still further pushed up η would substantially increase. But in the Otto engine, ρ cannot be increased beyond a certain value (about 5) otherwise the mixture would be fired during compression before the spark passes.

In the Diesel engine no gas or petrol is introduced during compression. The indicator diagram for the idealized Diesel cycle is shown in Fig. 13, all the processes being assumed to be quasistatic. In the first stage pure air is sucked in isobarically (EC in Fig. 13) and compressed adiabatically to about one-seventeenth of its volume (CD in Fig. 13). A valve is then opened, and oil or vapour is forced under pressure. The oil burns spontaneously as the temperature in the cylinder is about 1000°C. and above the ignition point of the fuel. The supply of oil is so regulated that during combustion, as the piston moves forward, the pressure remains constant. This isobaric burning of oil is represented approximately by the quasistatic isobaric process DA (as if the heat is absorbed from a series of external reservoirs ranging in temperature from T_d to T_a). At a certain stage, when the temperature has reached the maximum value, about 2000°K, the supply of oil is cut off. The piston is allowed to move forward, describing the adiabatic AB. At B a valve is opened, and the pressure drops to C. CE is the scavenging stroke,

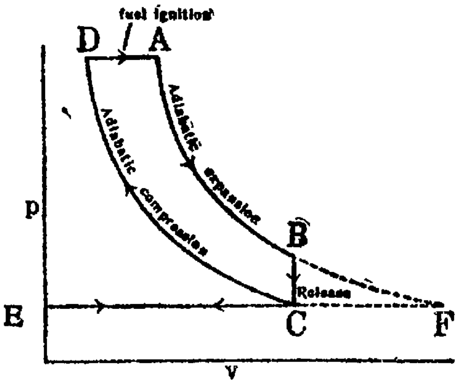

Fig. 13.—The Diesel Cycle.

in which the useless gas mixture is forced out, and the apparatus becomes ready for a fresh cycle.

The Diesel cycle can be performed in a cylinder of the type shown in Fig. 14. The cylinder is provided with the air inlet, the oil supply and the exhaust valves. The action of the cycle will be very clearly followed from the figure.

Instead of opening the valve at B we may allow the gas to expand as far as F when the inside pressure has fallen to atmospheric pressure, and the air mixed with the burnt gas to be forced out by a back stroke FC. As this would involve a rather large volume for the cylinder, this procedure is not adopted in actual practice.

We shall now calculate the efficiency of the Diesel engine, the maximum pressure, and the mean pressure. We shall first calculate the efficiency for the imaginary cycle AFCD.

Heat taken during DA $= C_p(T_a - T_d)$.
Heat rejected during FC $= C_p(T_f - T_c)$.

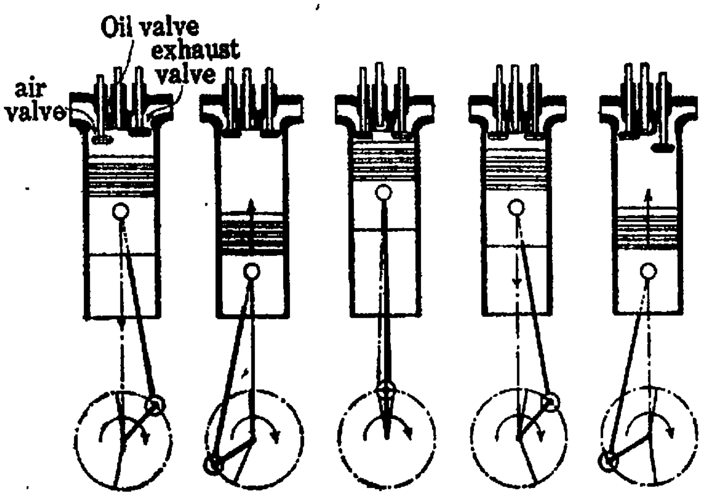

Fig. 14.—Strokes in a Diesel Engine.

(*a*) Beginning of suction stroke; air valve open.
(*b*) Beginning of compression stroke; all valves closed.
(*c*) Beginning of working stroke; oil valve open.
(*d*) Working stroke in progress. End of fuel injection; all valves closed.
(*e*) Beginning of scavenging stroke; exhaust valve open.

From the relation $p = cT^{\gamma/(\gamma-1)}$ (equation 30, p. 83) we have

$$\left(\frac{p_d}{p_c}\right)^{(\gamma-1)/\gamma} = \frac{T_d}{T_c} = \frac{T_a}{T_f} = \frac{T_a - T_d}{T_f - T_c}.$$

$$\therefore \eta = 1 - \frac{T_f - T_c}{T_a - T_d} = 1 - \left(\frac{p_c}{p_d}\right)^{(\gamma-1)/\gamma} \quad . \quad . \quad . \quad (26)$$

$$= 1 - \left(\frac{V_d}{V_c}\right)^{\gamma-1} = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \quad . \quad . \quad . \quad . \quad (27)$$

Thus the efficiency of the Diesel cycle is given by the same formula as for the Carnot or the Otto cycle. But in the Diesel engine the cylinder is designed for a maximum pressure of about 34 atmospheres. This determines the compression ratio because $p_a/p_c = \rho^\gamma = 34$. This gives $\rho = 12\cdot6$ and $\eta = 63$ per cent, which is a substantial improvement on the Otto engine. But as stated above, we have to take the cycle DABC. Hence heat is rejected at constant volume. We have heat rejected $= C_v(T_b - T_c)$.

$$\therefore \eta = 1 - \frac{C_v(T_b-T_c)}{C_p(T_a-T_d)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

4·19. Calculation of Efficiency and Mean Effective Pressure.—We have now to express η and other quantities in terms of p_c, T_c, (atmospheric pressure and temperature), p_1 the final pressure and $T_a/T_d = x$, because work done depends upon the final temperature (2040°K). It can be shown from the gas laws that

$$T_d = T_c \rho^{\gamma-1} = (340)\ (12\cdot6)^{\cdot39} = 915°\text{K}.$$

$$x = T_a/T_d = 2\cdot23.$$

$$T_b = T_c x^\gamma \doteq (340)\ (2\cdot23)^{1\cdot39} = 1037°\text{K}.$$

Now work done during each cycle

$$= C_p(T_a - T_d) - C_v(T_b - T_c)$$

and

$$\eta = 1 - \frac{C_v}{C_p}\frac{T_b - T_c}{T_a - T_d} = 1 - \frac{(x^\gamma - 1)T_c}{\gamma(x-1)\ T_d}$$

$$= 1 - \left(\frac{1}{\rho}\right)^{\gamma-1}\frac{x^\gamma - 1}{\gamma(x-1)}.$$

We thus see that for $x \to 0$, $\eta = 1 - (1/\rho)^{\gamma-1}$, otherwise it is slightly less. For the present case $\rho = 12\cdot6$, $x = 2\cdot23$.

$$\therefore \eta = 1 - (\cdot37)\ (1\cdot2) = \cdot556.$$

Thus the efficiency is reduced from 63 to 55 per cent, but this figure is still larger than the efficiency factor for the Otto engine.

Amplitude of volume change $= V_c - V_d = V_c\left(1 - \frac{1}{\rho}\right)$.

Output of work $= C_p\,(T_a - T_d)\,\eta$.

$$p_m = \frac{7}{2} p_c \rho^\gamma \left[(x-1) - \left(\frac{1}{\rho}\right)^{\gamma-1}\frac{x^\gamma - 1}{\gamma}\right]\Big/(\rho - 1) = 6\cdot96 \text{ atmos.}$$

and

$$\frac{p_a}{p_m} = \frac{34}{6\cdot96} = 4\cdot9.$$

The ratio has almost the same value as for the Otto cycle.

The Diesel engine therefore consumes less fuel than the Otto engine, but as it has to withstand a higher pressure it must be more robust. Also the mechanical difficulties are much greater, but they have been successfully overcome.

4·20. Semi-Diesel Engines.—We have seen that in Diesel engines a large compression ratio (12 to 1) is employed and the maximum pressure developed is enormous (35 atmos.); further a costly high-pressure air blast is necessary to force the liquid fuel into the cylinder. To avoid these the semi-Diesel engine, also called the *hot bulb engine*, was invented. In this the air is compressed to about 15 to 20 atmos. instead of 35 atmospheres. This air does not yet become hot enough to ignite the oil and is consequently passed through a hot bulb where it is heated by contact with the bulb to the required temperature. The hot bulb is simply a portion of the cylinder which is not cooled by the water jacket. It consequently becomes much heated and serves to heat the compressed air. Next the oil (fuel) is injected into this hot bulb where, by the combined action of the compressed air and the hot bulb, it ignites. For starting the machine the hot bulb must be heated by a separate flame. After a few cycles the bulb becomes hot and begins to function properly. Then the external flame is removed. The semi-Diesel engines now-a-days are generally two-stroke oil engines without the automatic control valves. The action of the two-stroke cycle is given in the next section.

4·21. Two-Stroke Engines.—It will be seen that in the Otto engine one stroke out of four is a working stroke; the engine therefore develops less power compared to its weight. To obviate this, Sir Dugald Clerk invented in 1880, the two-stroke engine, in which one stroke out of two is a working stroke and hence the power per stroke is doubled. This cycle requires a separate displacer or pump cylinder[1] in addition to the working cylinder. The working cylinder W has an inlet valve A (Fig. 15) and an exhaust valve B near its outward stroke. When the piston is at the end of its outward stroke the exhaust value is opened, and compressed gas from the compressing cylinder P enters the working cylinder, driving the products of combustion in front of it to the exhaust. In the backward stroke the exhaust valve is closed and the charge compressed.

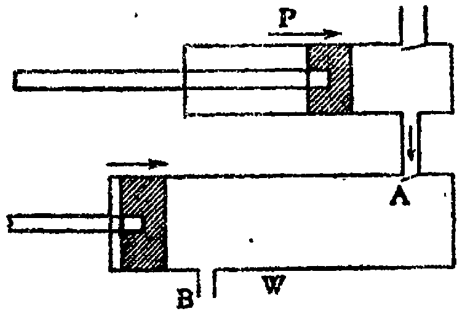

Fig 15.—Cylinder of a two-stroke engine.

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[1] In small two-stroke engines the separate cylinder is dispensed with and the charge is compressed in the crank case from where it enters the working cylinder later.

When the piston has almost reached the end of its journey the charge is fired. The piston is thrown forward giving us the working stroke. When the piston reaches the end of its outward stroke, a fresh charge is taken and the cycle begins afresh. The pump cylinder draws in a charge of gas and air and compresses it. The piston in the pump cylinder P is worked by the working piston by means of an eccentric.

The engine is of the constant volume type and the indicator diagram is similar to that of the Otto engine. Clerk engines are now extensively employed for high power stationary sources of energy as prime movers.

4·22. The "National" Gas Engine.—We shall now describe a typical Otto engine. Fig. 16 shows a 100 horse power "National" gas engine.

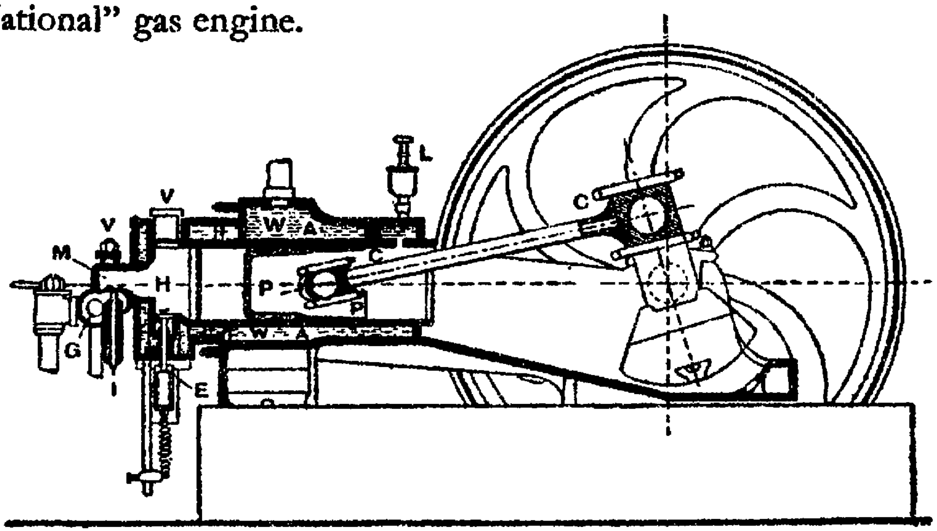

Fig. 16.—The "National" gas engine.

The engine is a stationary horizontal one having a single cylinder AA. The piston PP is attached to the crank-shaft by the connecting rod CC and fits gas-tight into the cylinder AA. H is the combustion chamber having the inlet valve I, the gas valve G and the exhaust valve E. The cylinder, the combustion chamber and the valve casings are cooled by the water jacket WW. L is the lubricator, V, V are plugs which may be removed to examine the valves. M is the ignition plug where a spark is produced by the "Magneto" and serves to ignite the charge. The various valves and the magneto are worked by suitable cams mounted on a shaft driven by the crank shaft.

The working of the machine is identical with that indicated in Fig. 11. The machine is started by rotating the fly-wheel so that the piston commences its outward stroke. An explosive mixture is introduced and ignited, and the piston is thrown forward. Then the working follows as indicated on p. 252.

4·23. Diesel Four-Stroke Engines.—These engines employ a cylinder and valves of the type shown in Fig. 14. In constructional design they are not much different from the Otto engine. They are further provided with a high pressure air blast for injecting the liquid fuel.

4·24. The Fuel.—Some engines employ gaseous fuels the chief of which are coal gas, producer gas, coke-oven gas, blast-furnace gas, water gas and natural gas (chiefly methane). The common liquid fuels are petrol, kerosene oil, crude oil, benzol and alcohol. In the Otto engine, if liquid fuel is used, it must be first vaporised and then admitted. Diesel engines generally employ crude oils and hence their fuel is very cheap.

During the brief period of fifty years the internal combustion engines have been much developed and employed for a variety of purposes. The steam engine, we have seen, is very wasteful of fuel, but the internal combustion engine is much more economical and has consequently been much employed.

The Otto four-stroke engine is employed in automobiles and aeroplanes. Petrol vapour is used as fuel in both cases. In aircraft engines the incoming air is usually compressed by a *supercharger* (which is essentially an air pump of some sort for increasing air density and pressure) and then fed into the engine. Four-stroke Diesel engines are largely employed in driving ships. Where very large power is necessary, the two-stroke Diesels are in common use. Diesel engine is more efficient and more economical of fuel. Still has combined a steam engine with a Diesel engine and has obtained much greater efficiency in steam locomotives (Still-Kitson locomotives).

Problem. Calculate the efficiency of a Diesel engine for which the adiabatic compression ratio $r_c = 17$, the adiabatic expansion ratio $r_e = 5$, and $\gamma = 1 \cdot 4$.

[From Fig. 13 we have the relations

$$\frac{T_d}{T_c} = \left(\frac{v_c}{v_d}\right)^{\gamma-1} = r_c^{\gamma-1} \; ; \; \frac{T_a}{T_b} = \left(\frac{v_b}{v_a}\right)^{\gamma-1} = r_e^{\gamma-1}$$

$$\frac{v_d}{T_d} = \frac{v_a}{T_a} \; ; \; \frac{v_d}{v_a} = \frac{r_e}{r_c} \text{ since } v_b = v_c.$$

Hence (28) yields

$$\eta = 1 - \frac{1}{\gamma} \frac{(T_a/r_e^{\gamma-1}) - (T_d/r_c^{\gamma-1})}{T_a - T_d} = 1 - \frac{1}{\gamma} \frac{r_e^{1-\gamma} - r_c^{1-\gamma} . \, v_d/v_a}{1-(v_d/v_a)}$$

$$= 1 - \frac{1}{\gamma} \frac{1/r_e^{\gamma} - 1/r_c^{\gamma'}}{1/r_e - 1/r_c} = 1 - \frac{1}{1 \cdot 4} \frac{1/5^{1 \cdot 4} - 1/17^{1 \cdot 4}}{1/5 - 1/17} = 0 \cdot 56].$$

STEAM TURBINES

4·25. The Steam Turbine.—We shall now give a brief description of the engines belonging to the windmill type. Windmills are set in motion by the impact of wind on the vanes of the mill, and at first sight it may appear strange why they should be classed as heat engines. But a little reflection will show that the wind itself is due to the unequal heating of different parts of the earth's surface, hence the designation is justified. But wind-power is rather unreliable, hence steam turbines were invented in which the motive power is supplied by the artificial wind caused by high pressure steam. There are two types of turbines :— (1) the *Impulse Turbine* in which steam issuing with great velocity from properly designed nozzles strikes against the blades set on a turbine wheel and in passing through them has its velocity altered in direction. This gives an impulse to the wheel which is thereby set in rotation. (2) The *Reaction Turbine* is somewhat similar in principle to the Barker's Mill which, as a laboratory toy, has been known to generations of students. In this the wheel is set in rotation in the opposite direction by the reaction produced by a jet of steam issuing out of the blades set in the wheel.

Though the steam turbines are simple in theory, in practice great mechanical and constructional difficulties had to be encountered, but thanks largely to the efforts of De Laval, Curtis and most of all to Sir C. Parsons who may be described as the James Watt of the steam turbine, that the difficulties were successfully overcome. To-day the turbine is a prime mover of great importance and is almost exclusively used as the source of power for all large-power land stations for the generation of electricity and for propulsion of big ships. Their great advantage lies in the fact that instead of the reciprocating motion of the ordinary steam engine a uniform rotary motion is produced by a constant torque applied directly to the shaft. They are more efficient than other engines because in them there is no periodic change of temperature in any part and so no heat is wasted. The full expansive power of steam can be utilised under suitable conditions. In America a turbine engine has been constructed which employs mercury vapour in place of steam and it is claimed that about 65 per cent. of heat energy is converted to work.

4·26. The Theory of Steam Jets.—The essential feature of the turbines is that in them the total heat (enthalpy) of steam is first employed to set the steam itself in motion inside the fixed nozzles or bladings (in reaction turbines) and this kinetic energy is utilised in doing work on the blades. The fixed nozzles are so designed as to convert most efficiently the internal energy of steam into its kinetic energy and produce a constant steam jet. We shall therefore first study the formation of jet under these conditions. We shall derive an expression for the kinetic energy imparted to the steam in traversing the fixed nozzle from the region of high pressure B (Fig. 17) to the region of low pressure C.

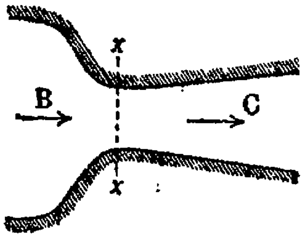

Fig. 17.—The fixed nozzle producing jet.

It will be observed that this is a *flow process* involving a *moving system* where a transformation of internal energy into external energy (kinetic and potential) and external work (or vice versa) takes place. In all our previous discussions with stationary or nearly stationary systems we considered only the internal energy, heat and work but in flow processes we must, in addition, take into account the kinetic and potential energies of the system. We shall therefore develop here a thermodynamic theory of all flow processes.

Let the pressure, volume, internal energy and velocity of steam in B per gram be denoted by p_1, v_1, u_1 and w_1 and the corresponding quantities in C by p_2, v_2, u_2 and w_2. Then the gain in kinetic energy of steam per gram on traversing the nozzle is $(w_2^2-w_1^2)/2J$ calories. The work done on steam in forcing it in B is p_1v_1 (since the pressure remains constant), while work done by steam against the external pressure in C is p_2v_2. The gain in internal energy of steam during passage is u_2-u_1. If in addition we assume that the heat Q is absorbed by the steam and shaft work W done by it, then application of the first law of thermodynamics to this flow process yields (neglecting any possible change in potential energy),

$$Q = u_2-u_1+p_2v_2-p_1v_1+W+\frac{1}{2J}(w_2^2-w_1^2). \quad . \quad . \quad . \quad (29)$$

In the case of the steam jet the process is adiabatic and no shaft work is done, therefore $Q = 0$, $W = 0$ and equation (29) yields,

$$\frac{1}{2J}(w_2^2-w_1^2) = p_1v_1-p_2v_2+u_1-u_2 = h_1-h_2, \quad . \quad . \quad (30)$$

i.e., the gain in kinetic energy is equal to the heat drop. Generally the initial velocity is sensibly zero and hence the kinetic energy of the issuing jet is given by the heat drop h_1-h_2.

In the case of turbines the change in kinetic energy is negligible and the process is nearly adiabatic, hence equation (29) yields,[1]

$$h_1-h_2 = W. \quad . \quad . \quad . \quad . \quad . \quad (30a)$$

We shall now calculate the heat drop h_1-h_2. If we assume that there is no loss of heat energy through friction or eddy currents in the nozzle, the heat drop h_1-h_2 is equal to the heat drop from the pressure p_1 to p_2 under isentropic conditions. This can be readily obtained from Mollier's diagram or from steam tables. It can also be calculated from the equation of state of steam.

We saw in §4·10 that under isentropic conditions the heat drop

$$J(h_1-h_2) = \int_{p_2}^{p_1} v\,dp. \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Callendar has shown that in a steam turbine the changes take place so rapidly that there is no time for condensation to take place at any stage so that the steam remains superheated or supersaturated. Under these conditions we can assume that pv^{γ} = constant, where γ is a constant and has the value 1·3. For the adiabatic expansion through the nozzle we have

$$\int_{p_2}^{p_1} v\,dp = \frac{\gamma}{\gamma-1}(p_1v_1-p_2v_2) = \frac{\gamma}{\gamma-1}p_1v_1\left[1-\left(\frac{p_2}{p_1}\right)^{(\gamma-1)/\gamma}\right] \quad (32)$$

We have then from (30), (31) and (32)

$$w = \sqrt{\frac{2\gamma}{\gamma-1}\left(1-p^{*(\gamma-1)/\gamma}\right)p_1v_1}, \quad . \quad . \quad . \quad (33)$$

where p^* denotes the pressure ratio p_2/p_1. The volume of steam per gram at any stage is from the adiabatic relation given by

$$v = v_1/p^{*1/\gamma}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

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[1] A third case is that of the throttling process (Chap. XII) where $W = 0$ and $h_1 = h_2$.

The volume of steam passing per second across any cross-section of area A is wA and the mass m passing per second is wA/v. From the condition of continuity this is the same at all sections of the nozzle. Hence the cross-section of the nozzle at any place should be given by

$$A = mv/w. \quad . \quad . \quad . \quad . \quad (35)$$

With the help of the foregoing relation we can calculate the velocity w, the volume v of steam and the cross-section A of the nozzle at any point for given values of the pressure ratio p^*. γ for dry superheated steam may be taken as 1·3 while for saturated steam $\gamma = 1{\cdot}135$. For wet steam $\gamma = 1{\cdot}035+0{\cdot}1q$ where q is the dryness. Callendar showed that actually the steam in a turbine remains in a metastable supersaturated state and γ may be taken to be 1·3.

q and w can be easily found out from Mollier's diagram. The values so obtained are given in table 1 in which initially dry saturated steam at 15 kg./cm.^{2} is taken.

Table 1.—*Velocity of steam jet and cross-section of nozzle for different exhaust pressures.*

p_2 kg./cm^2.	Dryness q	Volume in cubic metres for 1 kg.	Velocity in metres per sec.	Area of jet per kg. in sq. cm.
15	1	0·1360	0	
10	0·970	0·1933	400	4·83
9	0·963	0·2119	444	4·77
8	0·955	0·2347	492	4·77
7	0·946	0·2636	541	4·87
5	0·927	0·3538	644	5·49
1·033	0·856	1·430	957	14·94
0·12	0·784	9·85	1214	81·2

From table 1 it will be seen that both the velocity and the volume go on increasing as the pressure drop is increased. In the beginning the increase in volume is smaller than the increase in velocity while in the later stages it is much greater. Hence as the pressure drop increases the area A first decreases, then passes through a minimum and finally increases. The proper form of the nozzle for fully converting the heat drop into the kinetic energy of the steam is a convergent-divergent one, *i.e.*, the area of the section should at first contract to a narrow neck or "throat" and thereafter expand. This is the principle of the De Laval's convergent divergent nozzle (Fig. 18).

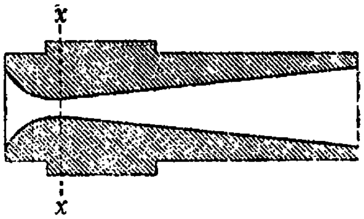

Fig. 18.—De Laval's convergent-divergent nozzle.

The throat is approached by a rounded entrance which allows the stream lines to converge. From the throat to the discharge end, the nozzle expands very gradually, usually in the form of a cone until it attains a sectional area suitable for discharging the steam at exhaust pressure. This area can be obtained from (35) after substituting the proper value of p^* in the expressions for v and w. The tapering is made sufficiently gradual to prevent the formation of eddies in the stream.

Let us calculate the dimensions of the throat. For maximum utility the nozzle should be so designed that the discharge per unit area per second, *viz.*, m/A at the throat is maximum. Now

$$\frac{m}{A} = \sqrt{\frac{2\gamma}{\gamma-1}\,\frac{p_1}{v_1}\left(p^{*^{2/\gamma}} - p^{*^{(\gamma+1)/\gamma}}\right)} \quad . \quad . \quad (36)$$

The condition of maximum is obtained by differentiating this expression with respect to p^* and putting it equal to zero. This gives

$$\overset{*}{p_t} = \left(\frac{2}{\gamma+1}\right)^{\gamma/(\gamma-1)} \quad . \quad . \quad . \quad . \quad . \quad (37)$$

which gives the pressure ratio at the throat. For $\gamma = 1{\cdot}3$ (dry steam), $\overset{*}{p_t} = 0{\cdot}545$. The maximum discharge from the nozzle is

$$m_t = A_t\left(\frac{2}{\gamma+1}\right)^{1/(\gamma-1)}\sqrt{\frac{2\gamma}{\gamma+1}\,\frac{p_1}{v_1}} \quad . \quad . \quad . \quad (38)$$

From these considerations it follows that if the exhaust pressure p_2 is less than $0{\cdot}545\,p_1$, the amount of discharge depends only upon the area of the throat and the initial pressure and not upon the back pressure. The divergent portion does not help to increase the discharge but merely gives additional velocity to the escaping steam by the further drop in pressure.

If the pressure ratio p^* is more than $0{\cdot}545$, *i.e.*, p_2 is more than $0{\cdot}545p_1$ the full velocity of the jet is obtained without the use of a divergent nozzle. In a Parsons' turbine the entire pressure drop is divided into many successive stages so that the pressure ratio in each stage is very large and hence the fixed channel producing the steam jet in Parsons' turbine is throughout convergent and has no divergent part (Fig. 24). Having considered the mechanism of the jet in detail we shall now study how the enormous velocity of the steam jet has been utilised in imparting rotation to the wheel.

4·27. The De Laval Turbine.—The velocity which is theoretically attainable in a steam jet is therefore enormous, and this causes extraordinary mechanical difficulties. For if we want to utilise the whole of this energy, by allowing the jet of steam to impinge on the blades or buckets of a turbine wheel, simple mathematical considerations to be given presently show that the velocity of the blades should not be short of one-half the velocity of the jet. Thus for maximum efficiency we should require to have a speed of the order of 1000 metres/sec. at the periphery of the wheel which carries the blades. The number of revolutions per minute necessary to produce such peripheral speeds for a wheel of moderate dimensions reaches the value of about 30,000 and such speeds are impracticable for two reasons. First, there are no constructional materials which can withstand such enormous peripheral speeds. The rotating parts would fly to pieces on account of the large centrifugal forces developed and there would be mechanical vibration of the rotating shaft. Secondly if the shaft is to be coupled to another machine which should usually rotate at a much lower speed, say 2000 r.p.m., the difficulties of gearing become almost insuperable. These were first successfully overcome by De Laval for low power turbines. For the gearing down, he used double-helical gear wheels with teeth of specially fine pitch. To enable the requisite peripheral speeds to be obtained with safety, the turbine wheel was made very thick in the neighbourhood of the axis (see Fig. 19) so that it can withstand the stresses set up by rotation, and further the shaft was made thin.

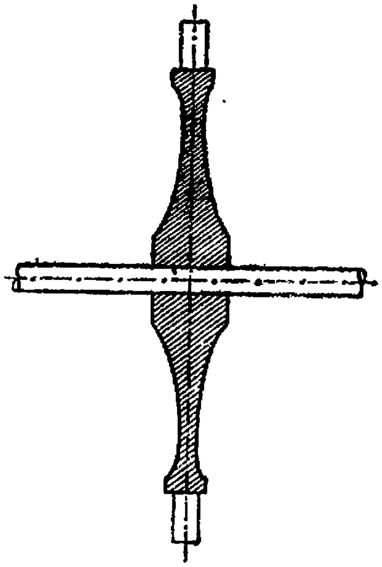
Fig. 19.—Vertical section of the wheel of De Laval turbine.

A De Laval turbine is illustrated in Fig. 20. The steam jet issuing from the fixed nozzles impinges on the blades, has its direction changed by them and thereafter escapes to the exhaust. Due to this action of the steam the blades are set in rotation. These are known as '*impulse turbines*' because the steam in passing through them is not accelerated but has only its direction changed. The interaction of steam with the blades is clearly indicated in Fig. 21 and the corresponding velocity diagram is shown in Fig. 22. In these turbines the blades are 'parallel,' *i.e.*, a passage between two blades has nearly the same cross-section everywhere so that the blades offer very little obstruction to the steam jet and hence the pressure of the steam remains practically the same on both sides of the wheel.

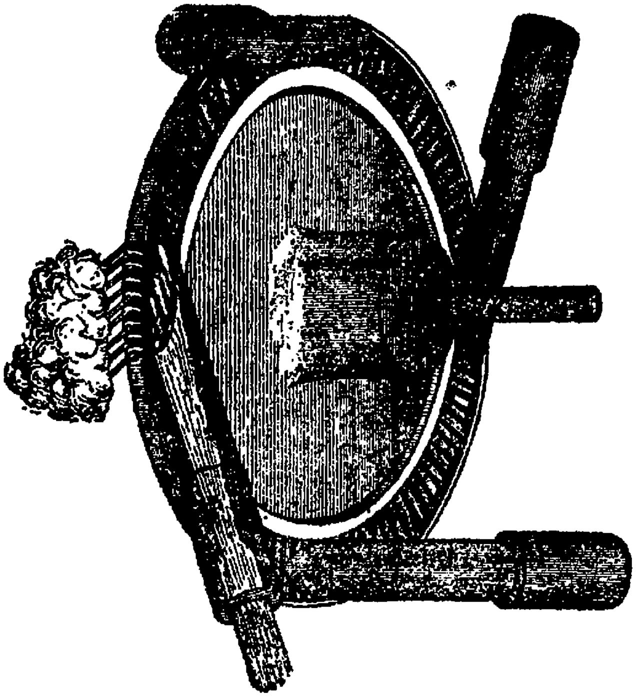
Fig. 20.—A De Laval turbine.

Suppose the jet enters the blades with the absolute velocity v_1 as indicated at an angle α. Due to the impulse the blade moves with the velocity u and hence the issuing jet has a velocity v_2 relative to the blade. Hence the inner surface of the blade at the extremity must be inclined at an angle β to the plane of motion of the wheel so that the steam may enter without shock. During the passage of the steam through the blade its relative velocity v_2 does not change in magnitude except for some friction which tends to reduce v_2. We may thus assume the relative velocity v_3 of steam at the exit to be equal to v_2. The corresponding absolute velocity will be v_4. Usually $\beta'=\beta$

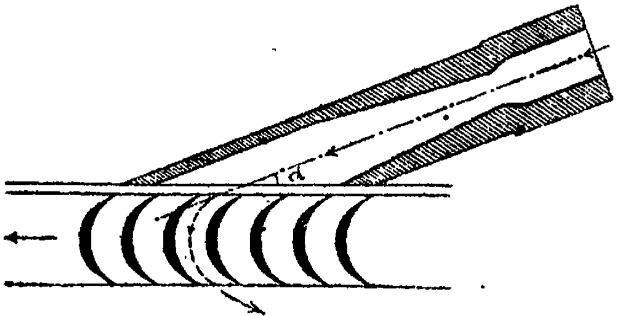

Fig. 21.—Action of steam on the blades of a De Laval turbine.

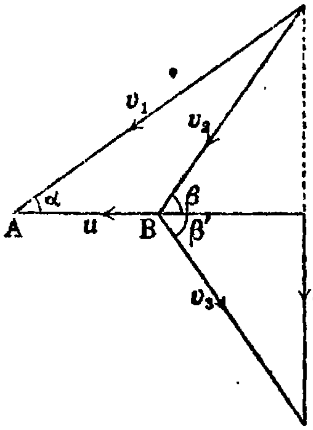

Fig. 22.—The velocity diagram of a De Laval turbine.

in order that the resultant impulse on the wheel acts in the plane of the wheel.

The most favourable speed of running will be that for which the velocity v_4 is perpendicular to the plane of the wheel and is very small, for v_4 would then be of no value in rotating the blade. It is easily seen that for this to be true u should be equal to $\frac{1}{2}v_1\cos\alpha$. For, from the law of compounding of velocities we have

$$v_4 = v_3 \sin \beta' = v_2 \sin \beta = v_1 \sin \alpha.$$

Also from the figure $\qquad AB = BC = u.$

$$\therefore u = \tfrac{1}{2}v_1\cos\alpha. \qquad . \quad . \quad . \quad . \quad (39)$$

The efficiency of the machine is

$$\frac{v_1^2 - v_4^2}{v_1^2} = 1 - \sin^2 \alpha, \qquad . \quad . \quad . \quad . \quad (40)$$

when shock and friction are assumed to be absent. In practice α is about 20° and hence efficiency $= \cdot 883$.

In the ideal case $\alpha = 0$, $u = v_1/2$, and efficiency $= 1$. Thus all the available heat drop is utilised in rotating the wheel and the efficiency corresponds to that of the Rankine cycle.

4·28. Division of the Pressure Drop into Stages. Rateau and Zölly Turbines.—As a prime mover, the De Laval turbine is quite efficient for producing low power. For generating high power, superheated steam must be used so that the pressure drop in the jet would be enormous, and hence for maximum efficiency the blades must move with very high velocity. Such large velocities are incompatible with safety. For this reason, the entire pressure drop is divided into a number of *stages*. Each stage consists of one set of fixed nozzles and one ring of moving blades mounted on a wheel fixed to the shaft. Across each stage, the pressure drop is small so that the blade velocity necessary for maximum efficiency is considerably reduced and can be easily attained in practice. This principle of *pressure compounding* was first given by Parsons and later adapted by Curtis, Rateau, and Zölly to the De Laval type. Rateau turbine has 20 to 30 stages, Zölly has about 10.

Principle of Velocity Compounding

4·29. The Curtis Turbine.—This is an impulse turbine but the kinetic energy of the jet is extracted not by a single ring of moving blades as in the De Laval type but by a series of two or more such rings. Between the first and the second moving rings there is a fixed ring of guide blades (Fig. 23). The action of the fixed guide blades is simply to alter the direction of the steam jet in such a manner that it may suitably give impulse to the next ring of moving blades, There is no drop of pressure either in the guide blades or in the moving blades. Now if the moving blades move with moderate velocity, the steam jet striking the first ring of moving blades loses only a part of its kinetic energy and possesses a large though reduced absolute velocity even when it leaves them. This velocity remains unaltered during its passage through the guide blades. The steam with its reduced velocity strikes the next ring of moving blades and gives them impulse. Thus the kinetic energy of the jet is extracted in steps and so the blades need have only a moderate velocity. *This principle of velocity compounding* was first introduced by Curtis and is the characteristic feature of Curtis turbines which are essentially multi-impulse turbines. In addition to this the principle of pressure compounding is also generally utilised in the design of Curtis turbines. There may be two or three stages of pressure drop, the kinetic energy in each stage being extracted in three or four steps. Thus the steam issuing out at the bottom in Fig. 23 passes through another set of fixed nozzles, acquires velocity and this kinetic energy is again extracted in steps.

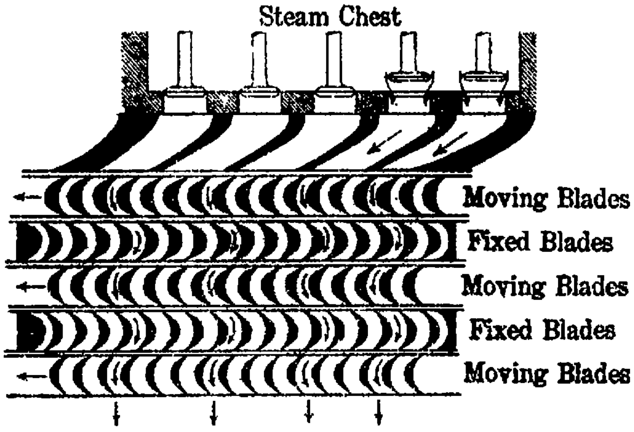

Fig. 23.—The Curtis turbine (velocity wheel).

4·30. Reaction Turbines—Parsons' work.—Parsons began his researches on steam turbine about the same time as De Laval (1884), but he did not accept the latter's solution of the problem, and went on with his own investigations which were completed by about 1897. His researches resulted in the evolution of a completely new type—the so-called *Reaction Turbines.* The mechanism of this type is shown in Fig. 24.

The essential feature of the Parsons' Turbine is its blading system. This consists of alternate rings of a set of fixed blades mounted on the inside of the cylindrical case or the stator, with a set of moving blades mounted on the shaft or the rotor, arranged between each pair of rings of fixed blades as shown in Fig. 24. There are no separate nozzles for producing a jet but the fixed blades act as nozzles. It will be noticed that the blades have convergent passages, *i.e.*, the cross-section of the passage goes on decreasing towards the exit side.

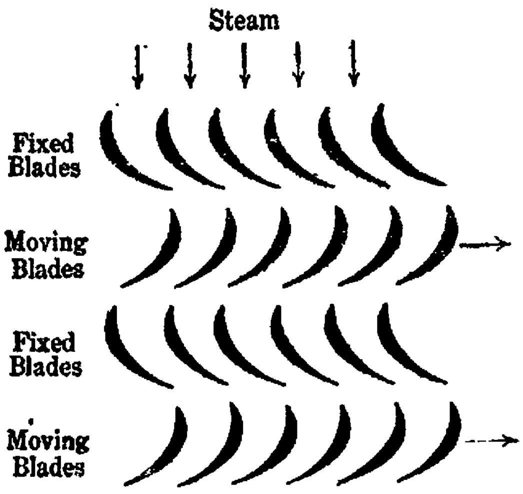

Fig. 24.—The blading system of a reaction turbine.

As the steam passes through the moving blades, there is a drop of pressure in consequence of which the steam jet increases in velocity as it traverses the blade-passage, and as it issues out, a backward *reaction* is produced on the blades which consequently begin to revolve. The steam then again passses to the next set of fixed blades where it again acquires velocity and enters the next set of moving blades nearly perpendicularly.

The moving blades are secured in grooves on the rotor shaft with their lengths radially outwards and parallel to each other. The fixed blades are secured in grooves in the enclosing cylinder and project inwards almost touching the surface of the spindle. The steam is admitted parallel to the axis of the shaft (axial flow type). One pair of rings of moving and fixed blades is said to form a *stage*, and generally a turbine has a large number of stages.

Pressure Compounding.—On account of the peculiar form of the blade-passage, the pressure goes on falling rather slowly, so that the whole pressure drop is spread over a large number of stages which may amount to 45 or even 100. In consequence of this arrangement, the velocity of the jet is very small compared to that of the De Laval type, and the requisite blade speed is 100 to 300 ft. per sec. This reduction of velocity brought about by the distribution of available pressure over a large number of stages constituted the master-invention of Parsons which was also applied to other turbines with great advantage as already mentioned.

As we proceed from one stage to another the pressure goes on diminishing, consequently the specific volume of steam goes on increasing. This requires a larger passage-way for the discharge of steam which is secured in practice by using longer blades on the exhaust side.

The design brings in many mechanical and constructional difficulties such as design of the shaft, problem of leakage of steam over the tips of blades due to a fall of pressure in them, the balancing of longitudinal stresses, etc. For a full discussion of these problems, and the methods by which they have been overcome special treatises should be consulted.

The velocity diagram for the 'reaction' blading is shown in Fig. 25. v_1 is the absolute velocity of steam when it leaves the fixed nozzles, u the velocity of the blades and v_2 the relative velocity of steam with respect to the blades. For the moving blades to be actuated by pure reaction and not by impulse it is clear that v_2 should be normal to the plane of the revolving wheel and should be very small so that the steam is relatively at rest with respect to the moving blades, *i.e.*, $v_1 = u$. Actually it is found that for maximum efficiency the velocity ratio $u/v_1 =$ ·75 to ·95. The steam in passing through the moving blades becomes accelerated and has the final relative velocity v_3 with respect to the blades, its absolute velocity being v_4 which should again be very small and perpendicular to the plane of the wheel. Thus it would enter the next ring of fixed blades with negligible velocity, become accelerated finally attaining the velocity v_1 and then enter the next ring of moving blades with the relative velocity v_2. Thus the velocity diagram would repeat itself. This would be the pure reaction turbine. In actual practice however the steam enters the moving blades with some relative velocity giving it an impulse as in De Laval's turbine and so the turbine works partly by impulse and partly by reaction.

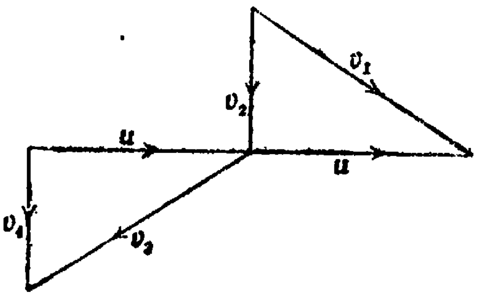

Fig. 25.—Velocity diagram of a pure reaction turbine.

From the above it will be seen that the distinction between 'impulse' and 'reaction' turbines is more popular than scientific and should not be taken too literally. All turbines are driven by 'reaction', due to the alteration of velocity of the steam jet in magnitude and direction. The real distinction between the two types is that in the 'impulse' turbine the reaction is due to the steam jet being slowed down while in the 'reaction' turbine working at unit velocity ratio the reaction is produced by the acceleration imparted to the steam in the moving blades themselves on account of the pressure drop. When the turbine works at a velocity ratio less than unity as is usual in practice the turbine utilises both these principles. Still however by simply looking at the blades one can say whether the turbine is of the 'impulse' or 'reaction' type, the impulse blading being characterised by parallel passages and the reaction blading by the convergent passages.

Most economical results are obtained when the ratio of the jet velocity to the blade velocity is 2·5. Generally the blades are so inclined that the steam issuing from the fixed blades makes an angle of 20° or 22° with the plane of the wheel.

4·31. Efficiency of Steam Turbines.—In the turbine we have seen that the kinetic energy of the jet developed by the pressure drop is equal to the drop in total heat $h_1 - h_2$ (equation 30). This is true as long as the expansion is adiabatic and reversible. Under this ideal condition the efficiency of the turbine (eqn. 30*a*) will be the same as that of an engine following the Rankine cycle. Actually however the process is not reversible. In the jet there is some friction between the fluid and the sides of the nozzle, and further eddies are formed which dissipate some kinetic energy of the jet into heat. This has a two-fold effect. The jet velocity is reduced by friction and is less than that given by the heat drop. Secondly the heat developed by the subsidence of the eddies goes to heat the fluid (or even re-evaporate a portion of the fluid if it has become wet) and thereby increases its volume and is available for reconversion into work but the reconversion is only partial. Thus the efficiency falls below the Rankine ideal.

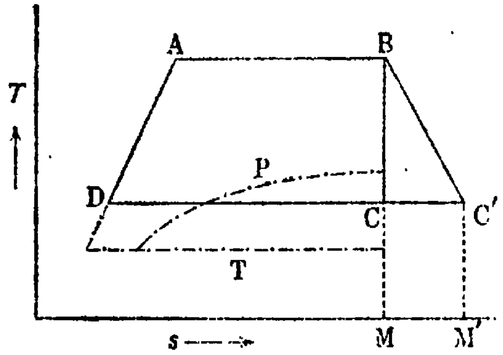

Fig. 26.—Entropy-temperature diagram of a turbine.

The effects can be well represented by the entropy-temperature diagram (Fig. 26) or the Mollier diagram (Fig. 27). On the entropy-temperature diagram the work obtainable from an ideal turbine with frictionless nozzle and using saturated steam is, from the first law, given by the area DABC minus the small amount of the work done by the feed pump, which may be neglected. Due to the presence of friction in the real case the expansion BC is not isentropic but is represented by some line BC′, and the heat developed by friction is equal to the area MBC′M′. Thus the net work obtained is area DABC′ − area MBC′M′ = area DABC − area MCC′M′ and is less than the work DABC obtainable from frictionless adiabatic expansion. The area CBC′ represents the work obtained from the heat developed by friction.

The behaviour on Mollier diagram is represented in Fig. 27. The steam entering the nozzle is in the state a_1. If the drop of pressure is from p_1 to p_2 the work obtainable by reversible adiabatic expansion is represented by a_1b_1 and is equal to the heat drop h_1-h_2. Actually however a portion of the heat drop is dissipated by friction. If this be known experimentally, say c_1b_1 the useful heat drop is a_1c_1 and the substance actually traverses the path a_1a_2 which may be supposed to be made up of the isentropic expansion a_1c_1 and the throttling process (Chap. XII) c_1a_2 in which the total heat remains constant.

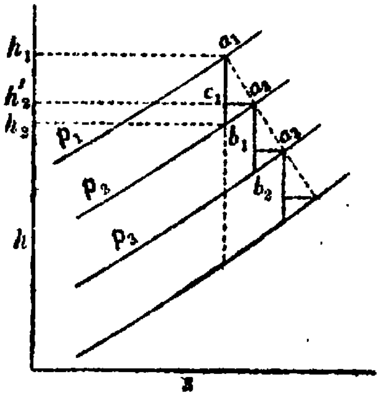

Fig. 27.—Mollier diagram for a turbine.

In a compound turbine the pressure falls in several stages, *i.e.*, from p_1 to p_2, from p_2 to p_3 and so on. The efficiency of the first stage is given by a_1c_1/a_1b_1, that of the second stage by a_2c_2/a_2b_2 and so on. $\eta_s = ac/ab$ is known as the stage efficiency. The total work done on the rotor is

$$\Sigma a_rc_r = \Sigma\eta_s \times a_rb_r = \eta_s \times \Sigma a_rb_r,$$

if η_s be assumed constant. In a compound turbine Σa_rb_r is greater than the total heat drop h_1-h_n. The ratio

$$R^* = \frac{\Sigma a_rb_r}{h_1-h_n} \quad . \quad . \quad . \quad . \qquad (41)$$

is called the *reheat factor*. The efficiency of the turbine as a whole is

$$\eta_t = \frac{\eta_s \Sigma a_rb_r}{h_1-h_n} = \eta_s \times R^* \quad . \quad . \quad . \quad . \quad . \qquad (42)$$

if η_s be assumed constant. η_t is thus greater than the stage efficiency η_s. Further in order to utilise the kinetic energy of the jet to the fullest extent, the moving blades must have suitable velocity. If the velocity is less the efficiency will be less. Thus the efficiency of the turbine falls if the blade velocity is decreased. When the pressure of the steam is great there is always some leakage and friction in the moving blades. This corresponds to a throttling process in which the pressure drops but the total heat remains constant and no useful work is obtained. This is why the turbine is less efficient than the reciprocating engine while using high pressure steam but it more than compensates for this in the low pressure region. In fact the efficiency of the turbine can be much increased by improving the exhaust vacuum as can be easily seen from Fig. 26. In this case the line CD is displaced downwards as shown at T. The corresponding case with the piston and cylinder engine is shown by the dotted line P in the same diagram. It is for this reason that in steam turbines there are arrangements for producing good vacuum in the condenser. On the same principles exhaust turbines are often employed to utilise the waste low pressure steam from a piston and cylinder type of engine.

Besides the ability to utilise low pressure steam there is another cause of the greater efficiency of the turbine. In the reciprocating engine the steam entering from the boiler into the cylinder has to heat the cylinder itself. Thus some heat is lost owing to the periodic changes in the temperature of the cylinder. This is avoided in the turbine. Further the turbine is preferred on account of its directly producing a uniform torque and due to its greater compactness. The efficiency of well designed turbines under favourable conditions is about 70 to 80 % of the Rankine ideal while in the reciprocating engine it is about 60%. Recently however still greater efficiency has been obtained with the turbine but due to its high speed of running it is often less convenient for low power work, because then its speed must be kept low when the efficiency falls down. In fact upto capacities of 10,000 k.w. the reciprocating engine is preferable but for capacities ten times greater, the turbine is the only choice as the size of the required reciprocating engine will be too large to be practical. Recently atomic energy obtained by the fission of fissile materials has been utilised to generate steam for running steam turbines for generating large power.

4·32. Alternative types of engines.—There are some other types of engines which have been tried with varying degrees of success. Among these, mention may be made of the 'internal combustion turbine' and the 'combustion propulsion' engines (the jet and rocket-propulsion systems).

In the *internal combustion gas turbine* high-pressure gases are used, instead of steam, to drive the blades of the turbine. During the past thirty years several designs of gas turbines have been invented and some have been placed on the market both as stationary engines and as locomotives on railways. In these the combustion of the oil used as fuel serves to heat the enclosed compressed air to a high temperature and high pressure, and this high pressure gas drives the turbine wheel. These engines possess several distinct advantages but the chief difficulty lies in finding sufficiently resisting substances to withstand these high temperatures.

The *jet propulsion system* has been developed in Germany and Italy mainly with the idea of devising a powerful means of propulsion for high-speed aircraft. Such a device utilising a *turbo-jet* is diagrammatically shown in Fig. 28. It consists of a compressor C and gas turbine T contained within a tube and connected to a common shaft S. A mixture of air and fuel is sucked in and compressed by the compressor and then ignited in the combustion space H so as to generate high pressure. This high pressure traverses the turbine where it gets accelerated and the pressure falls. The gas suffers further expansion in E and escapes at the rear of the machine with a high jet velocity V_j. The machine, on account of the reaction thus furnished, moves forward (towards the left in Fig. 28) with tremendous velocity which is, however, slightly decreased by the *ram drag*. The ram on the intake of gas, however, assists in the compression of the combustible mixture which is mainly done by the power obtained from the turbine.

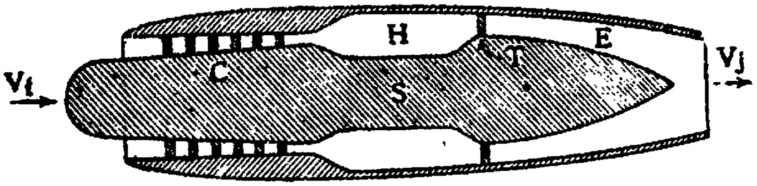

Fig. 28.—Principal elements of a turbo-jet.

If m is the mass of air flowing per second, V_j and V_i the relative jet velocity and the relative intake velocity respectively, the forward thrust F is, since pressure is equal to change in momentum per second,

$$F = m\,(V_j - V_i),$$

ignoring the small effect of fuel flow. The jet velocity V_j depends upon the temperature T_1 and pressure p_1 attained after combustion in the combustion chamber, and these depend upon the nature and composition of the combustion mixture. The burnt gas flows down the nozzle and expands to the exit pressure p_2, finally emerging with the absolute jet velocity w given by equation (33). The air flow, fuel flow and thrust can all be predicted theoretically as functions of speed of turbine, air speed and altitude and the agreement with experimental evidence is fairly satisfactory.

Mention may be made of the Rocket and the guided missile whose use by the Germans in World War II as V—2 rocket caught world imagination and whose potentialities for space travel are bound to make it an important tool of the future for scientific research. The essential difference between a rocket and a jet aircraft is that the former carries its own oxygen supply and thus can operate in vacuum while the latter obtains oxygen from the air. Unfortunately due to the military importance of the rocket its details are a closely guarded secret but the general principles are well understood. The fuel-propellant, solid or liquid, ignites producing a jet and the rocket takes off. The final rocket velocity $V_r = w \log_e M^*$ where w is the jet velocity and M^* denotes the ratio of the initial mass of the rocket to the final mass after combustion. In the two-stage rocket a smaller second rocket is placed in the nose which ignites a few minutes after take-off and the second rocket detaches itself and forges ahead under its own power with tremendous velocity. The two-stage rocket has attained velocities greater than 5000 miles per hour and heights exceeding 250 miles. A three-stage rocket has been planned to launch an artificial satellite of the earth.

PROBLEMS

1. Draw a tension-length diagram of a Carnot cycle for a wire when stretched.

2. Construct steam tables for total heat and entropy by utilising the values of p, v etc., given in the tables.

Books Recommended

1. Andrade—*Engines.*
2. Ewing—*Steam Engine and other Heat Engines.*
3. Glazebrook—*A Dictionary of Applied Physics*, vol. 1, Articles on Steam Engine; Engines, Thermodynamics of Internal Combustion; Turbines, Development of; Turbines, Physics of; etc.
4. *Handbuch der Experimental-physik*, vol. IX, part 2, pp 135—234.
5. Zemansky—*Heat and Thermodynamics* (1951), McGraw-Hill Book Co.
6. *Judge—Handbook of Aircraft Engines* (1945), Chapman & Hall Ltd.
7. Clarke—*Interplanetary Flight* (1952), Temple Press Ltd., London.

CHAPTER V

FIRST LAW OF THERMODYNAMICS

5·1. Introduction.—We have already introduced the subject of thermodynamics in a rather informal manner in the last chapter and have even stated the fundamental laws pertaining thereto. Since, however, thermodynamics like classical mechanics is an exact science, a more formal and rigorous presentation is called for. We shall therefore start with the subject *de novo.*

Thermodynamics is predominantly an empirical science based upon axioms whose validity has been established experimentally. The treatment of problems in pure or phenomenological thermodynamics is done wholly on the basis of such axioms or postulates. Just as in classical mechanics we start with a small number of premises or laws, like the Galileo-Newton laws of motion which are based on experience, and deduce other results therefrom; so in thermodynamics we infer the existence of certain fundamental laws from experimental evidence and then draw our conclusions from these fundamental laws. Pure thermodynamics is not concerned with attempts at seeking justification of these fundamental laws; this is generally done from the dynamic or kinetic point of view under a different branch of the subject called '*Statistical Thermodynamics*'.

Thermodynamical results are generally highly accurate and therefore the science of thermodynamics occupies an important place in the frame-work of modern physics. The laws of thermodynamics however require certain definite measurable quantities in terms of which they can be expressed, just as the laws of mechanics are expressed in terms of mass, distance, time etc. We shall now see how such quantities can be selected, properly defined and measured.

5·2. Scope of Thermodynamics.—Thermodynamics is mainly concerned with the transformation of heat into mechanical work or vice versa. At times we may have to take into account work done by electrical or magnetic agencies in the system or even the potential and the kinetic energy of the system as a whole, but in all cases the thermal energy (heat) or something depending on it has to be specifically involved. It is important to remember that in thermodynamics attention is focussed on the *interior* of the complex system in contrast to mechanics where attention is confined to the *external* aspects of the system. Consider for example, a rigid body. In mechanics, we describe the state of the body, by means of a few measurable quantities such as the position of the centre of mass, its velocity, acceleration, components of angular velocity etc. and express with their aid the kinetic and potential energies of the body as a whole. This may be said to constitute the *mechanical energy* of the body. In thermodynamics we disregard this external mechanical energy and the mechanical co-ordinates upon which it depends; instead we consider the interior of the system and find out by means of experiments some measurable quantities upon which the internal state of the system depends. Experiments show that the internal state of a chemically defined homogeneous body can be completely specified for all purposes with which thermodynamics is concerned, with the aid of two quantities, the volume V and the pressure[1] p, provided however, that the substance is in a state of equilibrium. The quantities p and V are called *variables of state* or *thermodynamic variables*.

The foregoing condition that the system must be in equilibrium, for making possible its complete description in terms of the variables of state, restricts the applicability of the science of thermodynamics to conditions of equilibrium of systems and to such processes which take place in states little different from the state of equilibrium. Thus thermodynamics is not applicable to any problem in which the rate of a process is under investigation, such as problems in dynamics, hydro-dynamics and chemical kinetics. It is applicable to all such equilibrium phenomena where heat plays a part such as change of phase, specific heat, radiation, chemical equilibria, electro-chemistry etc. etc.

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[1] In case of solids the assumption is generally made that the solid is subjected to isotropic pressure.

5·3. Thermodynamical Equilibrium.—A system suffers interactions with the surroundings and its internal state as determined by p, V changes. This is called *change of state*. In thermodynamics, the only possible interaction of a system with the surroundings that is permitted, is partly thermal and partly mechanical (dynamic); in other words all conceivable interactions consist only in a flow of heat from one to the other and the performance of work by the one on the other.

When there is no unbalanced force between the system and its surroundings and none exists between the different parts of the system itself, the system is said to be in a state of *mechanical equilibrium*. If the forces between the different parts of the system do not balance *i.e.* pressure is not uniform throughout the system, then turbulent motion, eddies etc. will be produced and the state of the system cannot be described without bringing in time. Similarly, if the force between the system and the surroundings is unbalanced, the system would have mass velocity and acceleration and time would again be involved in a specification of the state. Thus to describe a non-equilibrium state, time is a necessary factor.

If the temperature in all parts of a system is uniform and the same as that of the surroundings, the system is said to be in *thermal equilibrium*. If in addition the chemical composition is also the same throughout, it is said to be in *chemical equilibrium*. A system which is in thermal, mechanical and chemical equilibrium is said to be in *thermodynamic equilibrium*. It follows that the state of a system in thermodynamic equilibrium can be represented by specifying its p, V and the temperature T, quantities which are independent of the time. These are called *thermodynamic co-ordinates* or *variables of state*. A thermodynamic system is one which can be described in terms of thermodynamic co-ordinates and thus, of necessity, will be in thermodynamic equilibrium. A thermodynamic system may be chemical, magnetic, electrical etc. A *chemical system* is one having a fixed mass and exerting a uniform hydrostatic pressure on the surroundings provided that gravitational, electric, magnetic and surface effects can be neglected. A chemical system may be homogeneous or heterogeneous. A *homogeneous system* is uniform in every portion of it, with respect to its chemical composition as well as its physical condition. A *heterogeneous system* is composed of a number of homogeneous ones separated from one another by surfaces of discontinuity, each separate portion being called a *phase*, e.g. water contained in a closed vessel with vapour above the liquid, or a solution containing an excess of the solute. A *simple homogeneous system* is one whose internal state can be completely defined by the two parameters p and V. Examples of these are gases and liquids under equilibrium conditions, and solids in a state of isotropic stress, provided of course that gravitational, electromagnetic and surface effects are absent. We shall now undertake a detailed study of such simple systems in the following chapters, while mixtures of homogeneous systems as well as heterogeneous systems will be considered much later.

5·4. Zeroth Law of Thermodynamics.—In §1·1 we enunciated the law of thermal equilibrium with the help of which we introduced the concept of temperature. In the foregoing section we have already assumed that temperature is one of the quantities necessary to define the state of a thermodynamic system, in other words every thermodynamic system must possess a temperature. This postulate of the *existence of temperature* is sometimes called the *Zeroth Law of Thermodynamics*. The precise experimental basis for this assumption is the law of thermal equilibrium from which it can be shown that in a thermodynamical system for every participant in equilibrium, there exists a certain single-valued function f of the state variables p and V, which has the same numerical value for all the participants. This is mathematically expressed in the form

$$f_1(p_1, V_1) = f_2(p_2, V_2) = f_3(p_3, V_3) = \dots = t, \quad . \quad (1)$$

where the subscripts 1, 2 ... refer to the different participants. The identical numerical value has been put down as t which may be called the temperature, any one of the bodies being used as a thermometer reading the temperature t on a suitable scale. Thus equation (1) defines an *empirical temperature*. It is true that it has not been found possible to express eqn. (1) in finite or closed form for most substances. Its existence for most substances will however be taken for granted.

The methods of measuring this empirical temperature have already been fully explained in Chap. I. For the present, we are merely concerned with the concept of temperature and the fact of experience that an empirical temperature does exist, for all thermodynamic systems which can be measured in some agreed arbitrary manner. We shall take up in Chap. VI the question of measurement of temperature on a new and more fundamental basis (the Absolute Temperature).

5·5. The Thermal State of a Body and the Equation of State.—As mentioned above, the thermal state of a simple homogeneous body like a fluid or a solid in thermodynamic equilibrium is defined by its pressure p and the volume V. Equation (1) shows that t or the absolute temperature T is another thermodynamic variable or co-ordinate in terms of which the state of a system may be expressed. Equation (1) shows that out of the three thermodynamic variables p, V, T only two are independent and thus any two of these three are quite sufficient to specify the system completely. This also follows from the simple observational fact that the volume or temperature of any substance is perfectly definite when the other two quantities are known. Equation (1) is called the "equation of state" of the substance which may also be written in the more general form

$$f(p, V, T) = 0. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

An equation of state expresses the peculiar behaviour of one individual system in contradistinction to others and has always to be determined experimentally by actually measuring these quantities. The general thermodynamical theory, based on the universal laws of nature, is obviously incapable of yielding knowledge about one system as opposed to other, and hence cannot help us in theoretically deducing an equation of state. An equation of state must therefore be an experimental addition to thermodynamics, in no way deducible from the latter. As far as thermodynamics is concerned, this fact, that an equation of state does exist for all systems in equilibrium, is very important; it is immaterial whether or not we have enough knowledge to write it down mathematically. We may make here the otherwise obvious remark that the equation of state is not applicable to systems not in equilibrium; the pressure of a gas suffering unbalanced expansion cannot be calculated from the equation of state even if the volume and temperature are known.

5·6. Nature of Thermodynamical Variables.—We have assumed above that the state of a system is completely determined by specifying its thermodynamical variables V and T. These quantities refer to the gross characteristics or large-scale properties of the system—properties which can be more or less directly perceived by our senses. (The reader is already familiar with the methods of measuring p, V and T). These quantities may therefore be called *macroscopic (or large scale) coordinates* and serve to give a *macroscopic description* of the system. Thus a macroscopic description requires the specification of a few fundamental measurable properties of the system and requires no knowledge of the structure of matter composing the system. The macroscopic point of view has always to be reckoned with as it is very general requiring no assumption of any kind. This kind of approach is always employed in pure or classical thermodynamics where we do not care to enter into a detailed knowledge of the structure of the system, this knowledge being considered unnecessary and superfluous.

On the other hand, sometimes we want to be able to see in detail how things really work, and therefore like to supplement the macroscopic description by what is called the *microscopic* (or small scale) *description*. In this latter case, we postulate the existence of the molecules, their motions, collisions etc., the consequences of which we have considered in some detail in Chap. III. Supposing the matter consists of n particles, then we have to specify $6n$ quantities ($3n$ being coordinates of position and $3n$ being their velocities which however cannot be directly perceived by our senses and measured). But these assumptions may or may not be correct; their justification lies only in so far as the results obtained on that basis agree with the results deduced from the macroscopic view-point.

In the science of heat, we generally content ourselves with a macroscopic description of the system in terms of p, V, T since we have to consider matter in bulk consisting, even in the simplest case, of billions of particles and it is most inconvenient, if not impossible, to specify the position and velocity of every one of these molecules. The thermodynamic variables thus represent, in some way the average properties contributed by all the molecules of the system and have no meaning when applied to a group of very few particles. It is quite meaningless to talk of the pressure exerted by a single molecule or of the temperature of a single molecule. We can speak of the volume possessed by a single molecule, but this quantity bears absolutely no relation to the thermodynamic volume which denotes the whole space traversed by the molecules.

The question arises: how do the thermodynamical variables depend upon the behaviour of individual molecules? Attempt is sometimes made to offer an explanation in terms of the dynamical variables of the constituent particles. This was done in the Kinetic Theory of Matter (Chap. III). There we saw (p. 123) that the pressure exerted by a gas may be interpreted as the total impulse exerted per unit time by the impact of particles of the gas on unit area of the enclosing walls (eqn. 4). Temperature was shown to be a measure of the average kinetic energy of the molecules (eqn. 17) but really it is entirely a new concept and can be defined in an absolute manner only when we take up the second law of thermodynamics. For liquids and solids the kinetic theory is much less developed and the concepts of temperature and pressure cannot be easily explained in this way. In thermodynamics, however, we are only concerned with the energy changes and the initial and final states and not with the nature of molecular mechanism by means of which the change is brought about. Hence the methods of thermodynamics are very general and the results attained therefrom, remain true, whatever the mechanism of the change.

A necessary consequence of the incomplete macroscopic description employed in thermodynamics is that the future behaviour of the system becomes somewhat indeterministic giving rise to fluctuations, in striking contrast to the behaviour of dynamical systems which is perfectly definite and determinate. In classical mechanics the fundamental physical variables are time, space and mass, and the dynamical variables (position co-ordinates and momenta of the constituent particles) as well as the forces can be very accurately defined in terms of these, and once these are known, the subsequent career of the system can be uniquely and unequivocally worked out from dynamical principles. In thermodynamics, however, we are given only two macroscopic quantities (instead of the $6n$ dynamical variables), these being the statistical average effect produced by the $6n$ quantities and capable of being realised by various possible combinations of those $6n$ terms. Thus due to the indefiniteness of specification of the initial dynamical state (though the macroscopic state is definite) a complete indeterminacy of the resulting dynamical state is produced which does produce some, though not considerable, indeterminacy of the resulting macroscopic state giving rise to the so-called fluctuations. For further discussion of this point see Chap. IX.

5·7. Mathematical deductions from the Equation of State.—The form of equation (2) is known accurately for a perfect gas only (Chapter I). But though (2) is generally unknown, we can proceed a good deal towards studying the behaviour of a substance under different conditions by using differential expressions. We may imagine equation (2) to be solved out and written in the form

$$p = f(v, T). \qquad (2a)$$

From this we have on differentiation[1]

$$dp = \left(\frac{\partial p}{\partial v}\right)_T dv + \left(\frac{\partial p}{\partial T}\right)_v dT, \qquad (3)$$[2]

where $(\partial p/\partial v)_T$ denotes the rate of increase of pressure with increase of volume when the temperature is maintained constant, and $(\partial p/\partial T)_v$ denotes the rate of increase of pressure with increase of temperature when the volume is kept constant. In equation (3) the system is assumed to perform an infinitesimal process from one state of equilibrium to another. The differentials dp, dv and dT are therefore differentials of actual quantities or functions and are called *exact differentials* or *perfect differentials.* Further it should be emphasised in view, of what has been said in the last section regarding the nature of thermodynamical variables that the differentials dp, dv and dT—and in fact all infinitesimals in thermodynamics, should be very large in comparison to molecular fluctuations, so that they may include enough molecules to warrant the use of the macroscopic point of view but at the same time very small in comparison to p, v and T respectively.

It will be readily seen that $-v(\partial p/\partial v)_T =$ bulk modulus of elasticity in an isothermal process, or inverse of the coefficient of compressibility, and $\frac{1}{p}\left(\frac{\partial p}{T}\right)_v =$ coefficient of pressure increase in an isochoric or isovolumic process. Now for an *isobaric* or *isopiestic* (constant pressure) process $dp = 0$. Hence equation (3) yields

$$\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p \qquad (4)$$

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[1] This is a theorem in partial differentiation.

[2] If the further condition is imposed that $dT = 0$, (3) yields $1 = \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial p}\right)_T$, or $\left(\frac{\partial p}{\partial v}\right)_T = 1 \Big/ \left(\frac{\partial v}{\partial p}\right)$ which implies that the reciprocal of the partial differential coefficient is equal to the inverted coefficient.

Now $\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$ = coefficient of volume expansion in an isobaric process. Hence equation (4) shows that the isothermal bulk modulus, the volume coefficient of expansion and the pressure coefficient of expansion are not independent but are inter-related.

As an illustration, let us consider mercury at 0°C. and under atmospheric pressure. The coefficient of volume expansion $\alpha = 1\cdot 81\times 10^{-4}$ per °C. and the coefficient of compressibility β per atmosphere is $3\cdot 9\times 10^{-6}$. Hence from (4)

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \Big/ \left[-\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T\right] = \frac{1\cdot 81\times 10^{-4}}{3\cdot 9\times 10^{-6}} = 46\cdot 5 \text{ atmos.}$$

and the pressure coefficient

$$\frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_v = 46\cdot 5.$$

Assuming that the bulk modulus and the coefficient of volume expansion remain constant in the small temperature range, an increase of pressure by 46·5 atmos. will be necessary to keep the volume of mercury constant when its temperature is raised from 0°C. to 1°C.

The external conditions may be varied in quite other ways than those described above; for example, a gas may expand adiabatically. Then we get different relations which will be considered later.

Problems 1. (*a*) A block of copper at a pressure of 1 atmos. and temperature of 0°C is kept at constant volume. What will be the final pressure if the temperature is raised to 10°C.

(*b*) In the above problem if the volume also changes from an initial value of 1000 c.c. to 1000·1 c.c., what will be the final pressure. Assume that for copper the coefficient of volume expansion= 48×10^{-6} °C^{-1} and isothermal bulk modulus = $1\cdot 3\times 10^{12}$ dynes/cm.^{2} [*Hint.*—From Eqns. (3) and (4) we have

$$dp = \left(\frac{\partial p}{\partial v}\right)_T dv - \left(\frac{\partial p}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p dT = -\frac{\beta}{v}dv + \beta\,\alpha\,dT\Big].$$

2. An iron wire of cross-sectional area 0·01 sq. cm. and at a temperature of 20°C is stretched between two rigid supports on a sonometer board by means of a spring balance indicating a tension of 10^6 dynes. If the temperature falls to 0°C, calculate (i) the final tension, (ii) the frequency of vibration of the wire if its density is 7·8 gm./c.c. and the distance between the fixed supports is 1 metre. Assume that the coefficient of linear expansion = 12×10^{-6} per °C. and Young's modulus = 20×10^{11} dynes/cm.^{2}

[*Hint.* The pressure on the wire and its volume may be assumed to be constant. The state of the wire thus depends upon its temperature T and its length l, the latter being related to the tension F by Hook's law. Hence $F = f(l, T)$, and analogous to (4) we have

$\left(\frac{\partial F}{\partial T}\right)_l = -\left(\frac{\partial F}{\partial l}\right)_T\left(\frac{\partial l}{\partial T}\right)_F = -A\mathscr{Y}\lambda$ where A = cross-sectional area, $\mathscr{Y}$ = isothermal Young's modulus and λ = coefficient of linear expansion.]

5·8. The Forms of Energy. Total Energy of a Thermodynamical System.—As Thermodynamics is largely a study of energy-relationships, we make a preliminary survey of the forms in which energy is manifested in different classes of natural phenomena. We may enumerate the following forms with which the student must have become familiar:

1. Mechanical Energy, due to motion (kinetic), and due to position (potential), which arises from the existence of a field of force.
2. Internal mechanical energy which manifests itself as heat.
3. Chemical Energy.
4. Radioactive Energy, or more generally Nuclear Energy.
5. Electrical Energy.
6. Magnetic Energy.
7. Energy of Radiation.
8. Surface Energy (surface tension).

Of these different forms, the first two engage our special attention, firstly because the object of Physics so far has been largely to resolve all forms of energy to motions and positions of ultimate particles, and secondly, all forms of energy have a tendency to be dissipated as heat.

As is well-known from mechanics, the total energy of a dynamical system consists of kinetic energy due to its motion, and potential energy due to its position with reference to a fixed level. Thus for a particle moving in the gravitational field of the earth, the kinetic energy is $\frac{1}{2}mv^2$, and the potential energy is mgh. It is also well known that during the motion of the particle the sum of the kinetic and potential energies remains constant. This theorem is generalized in dynamics. If a system of bodies moves in a non-dissipative field of force, the sum of their kinetic and potential energies remains constant during the whole course of motion. Examples of these are the motion of planets round the sun, the motion of a pendulum, etc. provided friction is absent. This result is known in dynamics, as the *Principle of Conservation of Energy*, which was originally formulated for conservative mechanical systems, and later extended to include electromagnetic forces.

In a dissipative system, according to mathematical principles, energy is lost by friction. But physics tells us that there is no loss of energy as a whole. We have seen in Chap. III that when motion is dissipated by friction, an amount of heat appears, which is proportional to the amount of mechanical energy lost. Hence we conclude that kinetic energy has been only converted into heat energy, the total energy remaining constant.

The principle can be extended to other forms of energy. Electrical energy can be transformed to heat or to mechanical energy, but there is always an exact proportionality between the different forms of energy. This is the principle of Conservation of Energy in a general form. It follows[1] from a result of human experience which may be stated as a postulate in this form :—

"It is impossible to design a machine which will create energy out of nothing and produce perpetual motion. Energy can only be transformed from one form to the other."

5·9. Work.—Suppose a system interacts with the surrounding and passes from one state to another. In a thermodynamical system the interactions that are permitted are (1) by the performance of work and (2) by the transfer of heat. This work done by or on the system is supposed to be such as can be brought about by the raising or lowering of a weight externally coupled by some device to the system or by any other external mechanical device. Thus work in thermodynamics is a macroscopic concept and can be measured in macroscopic coordinates. We may call it *external* work in contradistinction with *internal* work, which is the work done by one part of a system on another part of the same system and which does not constitute work in the sense of thermodynamics. An example of the latter is the work done by the forces acting between the molecules of a gas in the Joule expansion (§2·27). As shown in §4·4 the work (external work) done by a mechanical system is $\int p dv$, but in the case of electric or magnetic systems we may have to include work due to electric and magnetic agencies as well.

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[1] It may be deduced from the mechanistic theory of the Universe which assumes that all physical phenomena are ultimately mechanical in their nature and that all processes can be analysed into elementary attractions and repulsions between the smallest constituents of matter obeying dynamical laws. This view is however open to criticism and is not quite correct as revealed to us by a study of some elementary phenomena connected with the origin of radiation and the structure of matter which have been successfully tackled by quantum mechanics. Thermodynamics however, starts from the fundamental postulate stated above and does not attempt to prove it.

5·10. Internal Energy.—There are systems which may show no apparent mechanical energy, but may still be capable of doing work. They are said to possess *internal energy.* Consider for example a mixture of hydrogen and oxygen gas. The system as a whole is not moving and hence has no external or dynamical kinetic energy and further, its gravitational potential energy is not altered, but still the system can do mechanical work on explosion. This is due to the internal energy of the system. It is not the function of thermodynamics to find the source of this energy; it is enough for its purpose that such an energy exists. Thermodynamics seeks to measure this energy in so far as it may be possible. The kinetic theory of matter (Chapter III) however, shows that this internal energy consists of the kinetic and potential energies of the molecules, atoms, electrons, nuclei etc. of which the matter is composed.

Now let external forces act on a thermally insulated system which, in consequence, passes from the state A to state B and suppose the work $-W$ is done by these forces on the system. Let the energy of the system in the two states be U_A and U_B respectively. Assuming the dynamical principle of conservation of energy we have

$$U_B - U_A = -W. \quad . \quad . \quad . \quad . \quad (5)$$

Eqn. (5) serves to define the internal energy of a system. Since the laws of interaction between the components of a system are not known, its internal energy cannot be calculated in absolute measure. Eqn. (5) however may be used to measure changes of energy; or if we assume quite arbitrarily that the internal energy U_0 in a certain equilibrium state O is zero, the internal energy in the state B can be measured by the work $-W_B$ done on the system in transforming it from its assumed standard state O to the state B by an adiabatic process. This provides us with an empirical definition of the energy U_B of the system, viz.

$$U_B = -W_B. \qquad (6)$$

For the definition (6) to have any meaning it is essential that the work W_B which the system does in passing from the state B to the standard state O, should depend only upon the two states and not upon the path of the transformation[1]. We shall assume for the present that this is so, and therefore (6) enables us to define the internal energy. If in any case it is found experimentally that this property does not hold, then there must be other ways besides mechanical work by which energy has been exchanged between the system and its surroundings. These other ways will be called non-mechanical. Thus the *internal energy of the system is in all cases by assumption, a single-valued function of the variables of state.*

It may be remarked that the internal energy as measured with the help of (6), will be in error by an indeterminate additive constant U_0, the internal energy of the system in the standard O state. This is however immaterial as we are always concerned with energy changes so that this additive constant will cancel out.

5·11. Heat.—In the last section we have stated that there may be other ways besides mechanical work (including in this term work due to electrical or magnetic agencies) by which energy is transferred from or to the system. The energy received in all these other non-mechanical ways is called *heat*. This abstract definition of heat can be shown[2] to be identical with the elementary calorimetric definition which states that heat is the energy transferred between the system and its surroundings by virtue of a temperature difference only. Thus heat must be carefully distinguished on the one hand from work which is transfer of energy without a temperature difference, and on the other from internal energy which resides in the system, while heat either enters the system or leaves it.

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[1] Fowler and Guggenheim consider this statement itself as the first law of thermodynamics.

[2] See Fermi, *Thermodynamics* (1938), pp. 17-18, Blackie & Son Ltd.

A *source of heat* of a given temperature T is defined to be a body which is such that it can exchange heat but no work with its surroundings and remains at the temperature T throughout the process.

For a thermally insulated system we have from (5)

$$\Delta U+\Delta W=0, \qquad (7)$$

where $\Delta U = U_B-U_A$, and ΔW has been written instead of W for the work done by the system. If however, the system is not thermally insulated, some heat ΔQ will enter the system and therefore the net energy entering the system will be $\Delta Q-\Delta W$, ΔQ being the energy entering the system in forms other than work. From the principle of conservation of energy we have $\Delta U=\Delta Q-\Delta W$. Hence

$$\Delta U+\Delta W=\Delta Q, \qquad (8)$$

or

$$\delta U+\delta W=\delta Q$$

for an infinitesimal process. This provides a simple way of measuring heat.

5·12. First Law of Thermodynamics.—The First Law of Thermodynamics[1] is simply the principle of conservation of energy applied to a thermodynamic system. It has been formulated in various forms. In one form, we stated it in Chapters II and III which may be restated as follows:—

Whenever other forms of energy are converted into heat or vice versa, there is a fixed ratio between the quantities of energy and of heat thus converted. Eqn. (8) is another statement of the first law in a more mathematical form. In words it can be stated as follows:—*We can define a quantity, called the internal energy,*

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[1] The most satisfactory logical formulation of thermodynamics is that of Caratheodory (*Math. Ann.*, 67, 355, 1909), but is too abstract to be quoted here. For a simple account see Born, *Phys. Zeits.* 22, 282, 1921, or Chandrasekhar, *Introduction to the Study of Stellar Structure* (1939), Chap. I.

for any system which is a function of the state of the system only, the increase in internal energy of the system is equal to the sum of the work done on the system and the heat (measured in the same units) added to it. The work $\triangle W$ will be equal to $\int p\triangle V$ for a simple chemical system, but for surfaces, magnetic or electric systems other suitable terms are to be included in $\triangle W$ to take into account the work done by surface tension, magnetic or electrical agencies.

It will be noted that a complete statement of the first law comprises two assertions : (1) Heat is a form of energy, (2) Energy is conserved in thermodynamic systems. It must be emphasised that it is only with the help of the first law or the principle of conservation of energy that we are able to define the new variable of state—the internal energy.

APPLICATIONS OF THE FIRST LAW

5·13. Specific Heat of a Body.—We have seen that the internal energy as defined above is a single-valued function of the variables of state. Now in the case of a simple homogeneous body we have seen in §5·5 and §5·7 that any two of the variables p, V, T are sufficient to define its state uniquely. Choosing therefore V and T as the independent variables we have

$$U=f(V,\ T), \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where U and V refer to a gram-molecule of the substance.

Differentiating (9) we get[1]

$$dU=\left(\frac{\partial U}{\partial T}\right)_v dT+\left(\frac{\partial U}{\partial V}\right)_T dV. \quad . \quad . \quad . \quad (10)^2$$

For a perfect gas $(\partial U/\partial V)_T=0$ (§2·27), while for a gas obeying van der Waals' equation it can be shown (see Chap. VII) that $(\partial U/\partial V)_T=a/V^2$.

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[1] The quantity dU is a perfect differential of a function U of the variables defining the state of the body; we can therefore write dU instead of δU. In contrast with this the quantities, δQ, δW are not perfect differentials. This is readily seen from the indicator diagrams since the values of the quantities δQ, δW, depend upon the path of the transformation and not only upon the initial and final states. Hence we have denoted these changes by the infinitesimals δQ and δW.

[2] From the definition of C_v (Eqn. 13*a*) this yields for a perfect gas $dU=C_v\,dT$ since $(\partial U/\partial V)_T=0$. Integrating we get $U=\int_0^T C_v\,dT+U_0$ where U_0 is the so-called zero-point energy. If, as in the case of a perfect monatomic gas, C_v is independent of T we get $U=C_vT+U_0$.

If an amount of heat δQ be added to a thermodynamical system, say a perfect gas, which expands by a volume dV against the pressure p, we have from (8) by the first law

$$\delta Q = dU + p\,dV, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where δQ, dU are expressed in energy units.

Substituting for dU from (10) in (11) we get

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV + p\,dV, \quad . \quad . \quad . \quad (12)$$

and dividing by dT we have

$$\frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T}\right)_v + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\frac{\partial V}{\partial T}\,.$$

Now $\delta Q/dT = C$, the gram-molecular specific heat. This will have different values according to varying external conditions. If pressure be kept constant $(\delta Q/dT)_p = C_p$, the specific heat at constant pressure. Hence

$$C_p = \left(\frac{\partial U}{\partial T}\right)_v + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p\,. \quad . \quad . \quad (13)$$

Again if the heat δQ be supplied at constant volume we have from (12)

$$\left(\frac{\delta Q}{dT}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v = C_v \quad . \quad . \quad . \quad . \quad (13a)$$

by definition. Utilising this result in (13) we have for any substance

$$C_p - C_v = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p \quad . \quad . \quad . \quad (14)$$

For a perfect gas,[1] $\left(\frac{\partial U}{\partial V}\right)_T = 0$, $p\left(\frac{\partial V}{\partial T}\right)_p = \mathrm{R}$.

$$\therefore\ C_p - C_v = \mathrm{R}, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

as was deduced in §2·26. For any other case it is shown in Chap. VII that

$$p + \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v\,.$$

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[1] From Joule's experiments we know that the change in temperature $\triangle T$ during free expansion of a perfect gas is zero. Since for this process δQ and δW are equal to zero, equation (12) yields $C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV = 0$; or $\left(\frac{\partial U}{\partial V}\right)_T = -C_v\frac{dT}{dV}$. The experimentally observed result $dT = 0$ therefore implies that for a perfect gas $(\partial U/\partial V)_T = 0$.

It is easy to see that δQ, the heat added, cannot be determined from the initial and final states of the body; it is necessary to know how the heat has been added. Hence C, the specific heat has no significance unless the external conditions are prescribed. We have defined C_p and C_v, but there may be other processes, *e.g.*, adiabatic, where $\delta Q = 0$ and $C = 0$.

5·14. Work Done in Certain Processes.—The following expressions for work done in different processes have been already proved :—

(*a*) Work done by a perfect gas in isothermal reversible or quasistatic expansion is[1] (p. 232) equal to $RT\, ln\, (V_b/V_a)$.

(*b*) Work done by a perfect gas in reversible adiabatic expansion in which the temperature falls from T_1 to T_2 is (p. 232) equal to $R(T_1-T_2)/(\gamma-1)$.

(*c*) Work done on a solid, during a quasistatic isothermal increase of pressure is equal to $\int p dV$ where dV should be evaluated for the process. Now

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT = \left(\frac{\partial V}{\partial p}\right)_T dp,$$

since the change takes place at constant temperature. Substituting the isothermal bulk modulus $E_T = - V(\partial p/\partial V)_T$ we get for the work

$$\int p dV = -\int \frac{V}{E_T} p\, dp = -\frac{V}{2E_T}\left(p_f^2 - p_i^2\right),$$

if we neglect the small variation in V and E_T during the isothermal process, and p_i, p_f denote the initial and final pressures.

(*d*) In the case of a cyclic process the substance returns to its initial state and hence $dU = 0$. Equation (11) then yields $\delta Q = p\, dV$ *i.e.*, the heat absorbed by the substance is equal to the external work done by it during the cyclic process. Thus in Carnot's cycle, the work done during a cycle is equal to $Q_1 - Q_2$.

5·15. Discontinuous Changes in Energy. Latent Heat.—When a body is in the condensed state (solid or liquid) and is subjected to increasing temperature, the state may suddenly change from solid to liquid form (fusion), or from liquid to gaseous form (evaporation), or from one crystalline form to another (allotropic modification). In such discontinuous changes the energy also changes discontinuously (phenomena of latent heat). Let us consider the evaporation of 1 gram of water at 100°C. and 1 atmos. pressure. Using equation (11) we obtain

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[1] *ln* denotes natural logarithms, *i.e.*, logarithm to the base *e*.

$$L = u_2 - u_1 + p(v_2 - v_1), \quad . \quad . \quad . \quad . \quad (16)$$

where u_2, v_2 respectively denote the internal energy and volume of 1 gram of vapour, and u_1, v_1 the corresponding quantities for the liquid.

Equation (16) expresses the fact that the heat added is spent in two stages: (1) in converting 1 gram of water to 1 gram of vapour having the same volume, (2) in doing external work, whereby the vapour produced expands under constant pressure to its specific volume. $u_2 - u_1$ is sometimes known as internal latent heat and $p(v_2 - v_1)$ as the external latent heat. For water at 100°C, $v_1 = 1$ c.c., $v_2 = 1674$ c.c. (specific volume of saturated vapour). Hence

$$p(v_2 - v_1) = \frac{1 \cdot 013 \times 10^6 \times 1673}{4 \cdot 186 \times 10^7} = 40 \cdot 5 \text{ cal.}$$

Since $L = 538 \cdot 7$, we have $u_2 - u_1 = 498 \cdot 2$ cal.

It is often convenient to denote the different states of aggregation of the same substance according to the following convention:

[H_2O] denotes solid water (ice).
(H_2O) „ liquid water.
H_2O „ gaseous „ (steam).

The quantity taken is always a mol unless otherwise stated. At 0°C. the latent heat of evaporation of water was determined by Dieterici to have the value 594·8 cal. The latent heat at constant volume is easily found by calculation to be 564·8 cal. Then the symbolical equation

$$H_2O = (H_2O) + 10{,}170 \text{ cal.} \quad . \quad . \quad . \quad . \quad (17)$$

expresses the experimentally observed fact that the energy-content of a mol of H_2O (gas) at 0°C. exceeds the energy-content of a mol of H_2O (liquid) at 0°C. by 10,170 calories, the change taking place at constant volume. We have further

$$(H_2O) = [H_2O] + 1{,}430 \text{ cal.} \quad . \quad . \quad . \quad . \quad (18)$$

i.e. energy of a mol of liquid H_2O at 0°C exceeds the energy of a mol of ice at 0°C by 1,430 cal.

From equations (17) and (18) we have by addition

$$H_2O = [H_2O] + 11{,}600 \text{ cal..} \quad . \quad . \quad . \quad . \quad (19)$$

i.e., heat of sublimation of 1 mol of ice at constant volume is 11,600 calories. This is a consequence of the First Law applied to a physical process and can be easily verified.

5·16. First Law applied to Chemical Reactions.[1] **Hess's Law of Constant Heat-summation.**—The First Law can be extended to Chemical Reactions. Thus when 2 mols of H_2 and 1 mol of O_2 are exploded together in a bomb calorimeter, 2 mols of (H_2O) are formed, and 136,800 calories of heat are evolved. Allowing for the heat evolved in passing from the gaseous to the liquid state, we obtain from the First Law, since $\Delta Q = -117{,}000$ and $\Delta W = 0$.

$$2U_{H_2} + U_{O_2} - 2U_{H_2O} = 117{,}000 \text{ cal.} \qquad (20)$$

i.e., the energy of 2 mols of H_2 and 1 mol of O_2 exceeds the energy of 2 mols of H_2O by 117,000 calories. The cause of this diminution of energy is easy to comprehend from mechanics. When two particles m and m' approach from infinity within a distance r of each other, the total potential energy diminishes by Gmm'/r if the particles attract each other according to the law of gravitation. The chemical forces are not of gravitational but of electrical origin, and if the particles are charged oppositely, the diminution in energy is Kee'/r. In the case before us, when 2 molecules of H_2 and 1 molecule of O_2 approach each other, the potential energy continues to diminish, till a minimum is reached. Then 2 molecules of H_2O are formed, and the total decrement in potential energy is converted to kinetic energy of the molecules and ultimately to heat. This is a rough mechanical picture of the probable unit mechanism of the reaction but the actual process may be more complicated. However in thermodynamics we are not concerned with the mechanism of the process but only with the initial and final states which are defined by the thermodynamical variables.

Hess stated in 1840, before the First Law had been clearly formulated, that if a reaction proceeds directly from state 1 to state 2, and again through a series of intermediate states, then the heat evolved in the direct change is equal to the algebraic sum of the heats of reaction in the intermediate stages. This is an important law in thermo-chemistry and is known as Hess's law of Constant Heat Summation.

The law is illustrated by the following examples :—

$$\text{C (diamond)} + \tfrac{1}{2}O_2 = CO + 26{,}100 \text{ cal.} \qquad (21)$$

$$CO + \tfrac{1}{2}O_2 = CO_2 + 68{,}300 \text{ cal.} \qquad (22)$$

We have by adding

$$\text{C (diamond)} + O_2 = CO_2 + 94{,}400 \text{ cal.} \qquad (23)$$

This is verified by experiments.

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[1] For other thermo-chemical applications see the report by Rossini in *Chem. Rev.*, **18**, 233, 1936.

We take another example. Let the symbol $(LiOH)_{aq.}$ denote the solution of 1 mol of the substance. Then consider the following equations :—

$$2[Li] + 2(H_2O) = 2(LiOH)_{aq.} + H_2 + 106{,}400 \text{ cal.} \quad . \quad (24)$$

$$2[LiH] + 2(H_2O) = 2(LiOH)_{aq.} + 2H_2 + 63{,}200 \text{ cal.} \quad . \quad (25)$$

The energy evolved is very easily determined from solution experiments. If we subtract (25) from (24) we get

$$2\,[Li]+H_2 = 2\,[LiH]+43{,}200 \text{ cal.} \quad . \quad . \quad (26)$$

i.e., the heat of formation of two mols of [LiH] from [Li] and H_2 is 43,200 cal.

5·17. Energy, a Fundamental Physical Quantity.—Though energy is treated in classical mechanics as a derived quantity being expressed in terms of the fundamental quantities mass, length and time by the relation $E = ML^2T^{-2}$, investigations in physics carried from the beginning of the current century, have shown that it is essentially a fundamental physical quantity.

The basis of classical mechanics discovered by Galileo and developed by Newton and others was the assumption of the invariable or absolute nature of the three concepts of mass, length and time. Mass was regarded as an inherent attribute of matter and it was never suspected upto 1896 that it could vary with the state of motion or rest of the piece of matter under consideration. Space was regarded as Euclidean, *i.e.*, the position of any point was supposed to be expressible in terms of the distance from a set of coordinate axes fixed in the space. Time was regarded as uniform, invariable flux independent of any system of reference and of the state of motion or rest of the observer. But all these conceptions have been, to some extent, upset by the investigations of Einstein who showed that what we physically measure as mass, time and length are relative, *i.e.*, they depend upon the state of motion or rest of the observer. This is known as *the Principle of Relativity* and though the principle is not necessary for dealing with phenomena which used to form the subject-matter of classical mechanics, the same cannot be said when we treat of atomic phenomena or of events taking place in the heavens (cosmological problems).

One of the consequences of Einstein's theory is the equivalence of energy and mass. He showed that the two are identical and differ only in a constant, namely $E = mc^2$. Thus if we took our unit of time to be 3×10^{10} times smaller than a second, there would be no difference between energy and mass. According to this concept the total amount of energy in an atom of matter is colossal. For example the total energy of an atom of hydrogen $E = mc^2 = 1 \cdot 66 \times 10^{-24} \times 9 \times 10^{20} = 1 \cdot 5 \times 10^{-3}$ ergs; *i.e.*, the total energy contained in one milligram of hydrogen is equivalent to the energy obtained by burning about $2\frac{1}{2}$ tons of coal.

Does it mean that the energy of a particle at rest and the same particle in motion are the same? No, for according to Einstein the mass of a particle at rest is not the same as that in motion. In fact he showed that $m = m_0/\sqrt{1-v^2/c^2}$. Thus the excess energy of a particle in motion over the same at rest is $(m-m_0)c^2$, and this reduces to the well- known kinematical expression $\frac{1}{2}mv^2$ when the terms involving 4th and higher powers of v/c are neglected. But though this can be done in phenomena which we have come across in classical physics, we have to deal in atomic physics with velocities of the same order of magnitude as that of light and in such cases we cannot put the kinetic energy equal to $\frac{1}{2}mv^2$.

In recent years sufficient evidence has been accumulated to show that in the formation of the nuclei of atoms, the conversion of mass into energy takes place. Thus upto 1932 it was believed that the ultimate constituents of matter were the proton having a mass of 1·00759 (in terms of $O^{16} = 16$) and charge of $+e$ and an electron having the mass 0·00054 and charge $-e$, and nuclei of all atoms were supposed to be built up of these fundamental particles. Since 1932 however, it has been established that the nucleus is composed of protons and neutrons, the latter being a neutral particle of mass 1·00813 first discovered by Chadwick. Since all nuclei are supposed to consist of these elementary particles it may be expected that the mass of the nucleus will simply be equal to the sum of the masses of the constituent particles. Actually however the accurate measurements of Aston, Bainbridge and others show a slight difference, the mass of the nucleus being less. Thus the helium nucleus ${}_2He^4$ is supposed to be built up of 2 protons and 2 neutrons. Its mass has been determined accurately to be 4·00292 while the mass of 2 protons and 2 neutrons is equal to 4·03312. Thus in the formation of the He^4 nucleus, out of the fundamental constituents, a quantity of mass of matter $\triangle m = 0{\cdot}0302$ is lost. The same thing takes place in the case of formation of all other nuclei and there are reasons to believe that in the formation of complex nuclei out of fundamental particles the excess of energy as measured by the excess of mass of the constituent fundamental particles over that of the nucleus is given out in the form of radiation of frequency ν and energy $h\nu = \triangle m.c^2$. Thus in addition to the problems of conversion of the usual forms of energy into one another which are studied in classical physics, we have to study further the convertibility of mass into radiant energy. But the process is not unidirectional. The reverse process (*viz.*, the conversion of radiation into matter) was discovered in 1932 by C. D. Anderson and Neddermeyer who showed that radiant quanta possessing sufficient energy, *e.g.*, γ rays of ThC″ are split up into a pair of electron and positron on hitting the nuclei of heavy matter (*Electrofission or Materialisation of Quanta*). It is therefore evident that such processes, *viz.*, conversion of mass into radiant energy and *vice versa* play a great part not only in the formation of nuclei, but in fundamental cosmological problems such as maintenance of the energy of star, fate of radiation which is being poured into space by stars, etc. It is clear that when we have a better knowledge of such processes, we may expect a further extension and development of the methods of thermodynamics along these lines.

The most spectacular application of the law of equivalence of mass and energy is to be found in the discovery of the 'Atom Bomb' in 1945.

5·18. Supposed Violation of the First Law.—When the phenomenon of Radioactivity was first discovered towards the end of the last century, it was found that radium and other radioactive bodies were constantly evolving heat. It seemed as if radium was manufacturing energy out of nothing in violation of the First Law of Thermodynamics. Subsequent experiments however showed that there was no violation of the First Law. Radium emits α particles (swiftly moving positive particles, charge $2e$, mass $4M_H$, *i.e.*, mass of He-atom), β particles (very swiftly moving electrons) and γ rays (very penetrating X-rays). When these are stopped in their passage, their energy is converted to heat. The heat evolved by radium has been shown to be quantitatively equal to the energy of the α and β particles and of γ rays (*Vide, Modern Physics*, Vol. I, by Saha and Saha, p. 164). But why the nucleus goes on emitting α, β and γ rays spontaneously, remains unexplained from the mechanical point of view.

Problems

1. Assuming the expansion to be adiabatic, calculate the change in temperature when perfectly dry air rises up in the atmosphere.

[Use eqn. (40′) of Chap. III and eqn. (30) of Chap. II, and thereby obtain the relation $\frac{dT}{dh} = -\frac{\gamma-1}{\gamma}\frac{gM}{R}$].

2. Calculate the work done when 1 mol of a van der Waals' gas expands quasistatically and isothermally from a volume of 10 litres to 20 litres at 0°C, given that the van der Waals' constant $a = 1{\cdot}4 \times 10^{12}$ dynes $\times$ cm.^{4} and $b = 41$ c.c.

3. The pressure on a block of copper weighing 200 grams is increased quasistatically and isothermally from 0 to 300 atmos. Calculate the work done, given that the density of copper = 8·9 gm/c.c. and isothermal bulk modulus = $1 \cdot 3 \times 10^{12}$ dynes/cm.^{2}

Books Recommended

1. Planck—*Thermodynamics.*
2. Fermi—*Thermodynamics* (1938), published by Blackie & Son Ltd.
3. Ubbelohde, *An Introduction to Modern Thermodynamical Principles*, (1937), Clarendon Press, Oxford.
4. Zemansky, *Heat and Thermodynamics* (1951), McGraw-Hill Book Co.
5. Epstein, *Text-Book of Thermodynamics* (1937), John Wiley & Sons, New York.
6. Birtwistle, *Thermodynamics.*
7. *Handbuch der Physik*, Vol. 9.

CHAPTER VI

THE SECOND LAW OF THERMODYNAMICS AND ENTROPY

6·1. Scope of the Second Law.—The Second Law of Thermodynamics deals with a question which is not at all covered by the First Law, *viz.*, the question of direction in which any physical or chemical process involving energy changes takes place.

A few illustrations will clear the point. Let us consider the thermodynamic process illustrated by the symbolic equation :

$$2H_2+O_2 = 2H_2O+U \text{ calories.} \quad . \quad . \quad . \quad (1)$$

The equation tells us that if 2 mols of H_2 gas combine with one mol of O_2, 2 mols of H_2O-vapour are formed and U calories of heat are evolved, or *vice versa*, if 2 mols of H_2O-vapour are to be decomposed completely into H_2 and O_2, U calories of heat must be absorbed. This result is obtained as a matter of experience from calorimetric experiments, and we interpret the result according to the First Law of Thermodynamics by saying that in the combination of 2 molecules of hydrogen with 1 molecule of oxygen to form 2 molecules of H_2O, the diminution in energy amounts to $U/2N$ calories per molecule. This result can further be utilised in calculating energy relations in other reactions. But the first law cannot tell us in what direction the reaction will take place. If we have a mixture consisting of H_2, O_2 and H_2O-vapour in arbitrary proportions at some definite temperature and pressure, the first law cannot tell us whether some H_2 and O_2 will combine to form H_2O or some H_2O will dissociate into H_2 and O_2, the system thereby passing to a state of greater stability.

Or we can take a physical example. When two bodies, A and B, exchange heat, the first law tells us that the heat lost by one body is equal to the heat gained by the other. But it does not tell us in which direction the heat will pass. Only experience tells us that heat will pass from the hotter body to the colder *spontaneously*, but in speaking of hotter and colder bodies, we are making use of a new physical concept (*temperature*) which is not at all included within the scope of the first law. For giving us guidance in deciding the question of direction in which a process will take place, we require a new principle. This principle, the knowledge of which arose out of Carnot's speculations about the convertibility of heat to work, is generally known as the *Second Law of Thermodynamics.*

6·2. Different Formulations of the Second Law.— The problem of convertibility of heat to work has been treated in Chap. IV. It is readily observed that the main question was about the direction of energy transformation. Mechanical energy and heat are only different forms of energy, but while mechanical energy can be completely converted to heat by such processes as friction, it is not possible to convert heat completely to work. Even by using reversible engines which are the most efficient, only a fraction can be converted to work. The conversion is therefore only partial. The question is, why is it so?

An answer to this question has been given already in Chap. IV, *viz.*, if it were possible to design an engine more efficient than a reversible engine, we could continuously abstract heat from the colder of two bodies in a system and convert the whole of it to work, and the machine would go on running almost indefinitely. We could in this way convert into work the enormous stores of internal energy contained in the oceans, the atmosphere, the body of the earth, etc. and achieve a kind of perpetual motion which we call ***perpetual motion of the second kind*** as suggested by Ostwald. We are convinced as a result of our experience that such a perpetual motion machine which utilises the internal energy of only one heat reservoir or, in other words, works without temperature differences, is impossible of realisation. We may start from a statement which expresses this conviction of ours, just as the first law is based on the conviction that Energy cannot be created, but can only be transformed. We may make the statement in the following form which we may call the Kelvin-Planck statement of the Second Law :—

"*It is impossible to construct a Heat Engine which, operating in a complete cycle, will abstract heat from a single body, and convert the whole of it to work, without leaving changes in the working system.*"

Lord Kelvin stated the law in this form: "*It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.*"

Clausius stated it in the form[1]:—"*It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature, or heat cannot of itself pass from a colder to a warmer body.*"

The statements of the second law by Kelvin and Clausius given above necessarily imply that the working system undergoes no change in the process and the other bodies suffer no change other than that stated therein. We can start from either of these two statements and deduce the other, showing thereby that they are equivalent. It will be seen that these statements fix our attention on a machine or a complete process and not on the material undergoing the process.

A consideration of the problem from the viewpoint of the kinetic theory, enables us to grasp the real situation. According to the kinetic theory, heat consists in the random motion of the molecules of the body. When a wheel, moving rapidly, is brought to rest by friction with another body, then prior to stoppage, the particles of the wheel were all moving with identical angular velocity. When it is stopped, all this energy has gone to increase the random motion of the myriads of particles of which the wheel and the body against which it is moving, are composed. Therefore, by friction, ordered motion of particles has been converted to chaotic motion. Hence when we want to convert heat energy to mechanical energy, the problem is reversed; we have to make all the molecules move in the same direction with the same velocity, the sum-total of energy of ordered motion is to be equal to that of chaotic motion. The feat is not possible simply because we cannot deal with the molecules individually. Experience tells us that order always tends to degenerate spontaneously to chaos, and it requires effort to evolve order out of chaos. This aspect of the problem was discovered by L. Boltzmann and he showed how to calculate the value of chaos in terms of physical concepts, and interpret it in terms of known physical quantities. We shall take Boltzmann's theorem in Chap. IX.

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[1] It will be seen that this statement goes beyond the ordinary results of conduction. It states that we cannot completely undo the effects of heat conduction even in any indirect way.

6·3. Absolute Scale of Temperature.—Lord Kelvin[1] showed in 1848 that with the aid of the ideal Carnot engine, it was possible to define temperature in terms of energy, and the scale so obtained is independent of the nature of any particular substance. Kelvin started from the result (p. 241) that the efficiency of all reversible engines working between two temperatures is a function of the two temperatures only and is independent of the nature of the working substance. This may be mathematically stated in the form

$$W/Q_1 = f(\theta_1, \theta_2), \quad . \quad . \quad . \quad . \quad (2)$$

where W is the work done by the Carnot engine, Q_1 the heat taken in and θ_1, θ_2 the temperatures[2] between which the engine works.

Now $W = Q_1 - Q_2$ where Q_2 is the heat rejected. Hence

$$\frac{Q_1 - Q_2}{Q_1} = f(\theta_1, \theta_2),$$

or

$$\frac{Q_1}{Q_2} = \frac{1}{1 - f(\theta_1, \theta_2)} = F(\theta_1, \theta_2), \quad . \quad . \quad . \quad (3)$$

where F denotes some other unknown function.

It can be easily shown that the ratio Q_1/Q_2 can be expressed in the form $\psi(\theta_1) / \psi(\theta_2)$. For if we have reversible engines working between the pairs of temperatures (θ_1, θ_2), (θ_2, θ_3), (θ_1, θ_3), and the heat absorbed or evolved (as the case may be) at these temperatures be Q_1, Q_2, Q_3 respectively, then

$$\frac{Q_1}{Q_2} = F(\theta_1, \theta_2); \quad \frac{Q_2}{Q_3} = F(\theta_2, \theta_3); \quad \frac{Q_1}{Q_3} = F(\theta_1, \theta_3). \quad . \quad (4)$$

We have from the above

$$\frac{Q_1}{Q_3} = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3).$$

Hence the function F must satisfy the relation

$$F(\theta_1, \theta_3) = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3). \quad . \quad . \quad . \quad (5)$$

This condition will be satisfied only when $F(\theta_1, \theta_2)$ is of the form $\psi(\theta_1)/\psi(\theta_2)$ for it is only then that θ_2 will cancel out in the right-hand term of (5) as required by the left-hand term. Therefore for any reversible engine

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[1] *Phil. Mag.*, 1848; *Trans. Roy. Soc. Edin.*, 1854.

[2] These are the values of the temperature measured on any arbitrary scale.

$$\frac{Q_1}{Q_2}=\frac{\psi(\theta_1)}{\psi(\theta_2)}. \qquad (6)$$

It will be seen that if $\theta_1>\theta_2$, $Q_1>Q_2$ and therefore $\psi(\theta_1)>\psi(\theta_2)$, *i.e.*, $\psi(\theta)$ is a quantity which increases monotonically with θ and may be used to measure temperature. Denote the value of $\psi(\theta)$ by τ. The relation (6) then becomes

$$\frac{Q_1}{Q_2}=\frac{\tau_1}{\tau_2}. \qquad (7)$$

Equation (7) is used to define a new scale of temperature τ, which is called the thermodynamic or Kelvin scale. This scale does not depend upon the properties of any particular substance for equation (7) is universally true. The ratio of any two temperatures on this scale is equal to the ratio of the heats taken in and rejected by an engine working reversibly between the two temperatures.

The zero of this scale ($\tau = 0$) is that temperature at which $Q_2 = 0$ (from 7) and hence $W = Q_1$. Thus all the heat taken by the engine has been converted into work and the efficiency of the engine is unity. τ cannot be less than this, *i.e.*, negative, for if it were so, Q_2 would be negative which implies that the engine would be drawing heat both from the source and the sink. This is impossible from the second law and hence $\tau = 0$, is the lowest temperature conceivable. This is the thermodynamic definition of the absolute zero of temperature.

The zero having been determined, let us fix the size of the degree. In conformity with general usage we suppose that the interval between the freezing and the boiling points of water is divided into 100 equal parts on this scale, *viz.*,

$$\frac{Q_{\text{steam}}}{Q_{\text{ice}}}=\frac{\tau_{\text{ice}}+100}{\tau_{\text{ice}}}. \qquad (8)$$

The thermodynamic scale is thus completely defined and fixed. We have next to see how this scale can be realised in practice.

For this we must investigate the property of some actual substance. A perfect gas is very suitable for this purpose. In fact we have already shown on p. 233 that for a Carnot engine using a perfect gas as the working substance,

$$\frac{Q_1}{Q_2}=\frac{T_1}{T_2}, \qquad (9)$$

where T_1, T_2 are the temperatures measured on the perfect gas scale. Equation (7) combined with (9) yields

$$\frac{\tau_1}{\tau_2} = \frac{T_1}{T_2}, \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

i.e., the ratios of any two temperatures on the thermodynamic scale and the perfect gas scale are equal. Thus the absolute zero of the thermodynamic scale coincides with the zero of the perfect gas thermometer, for if $\tau_2 = 0$, $T_2 = 0$. Further from (8) and (10) since the interval between the ice point and steam point is 100° on both scales τ_{ice} and T_{ice} are identical, and in general from (10) other temperatures on the two scales are also identical. Thus the thermodynamic scale is given by the perfect gas thermometer. For the methods of reducing the ordinary gas scale to perfect gas scale see §1·7.

ENTROPY

6·4. Definition of Entropy.—The formulation of the Second Law, as in § 6·2, is not of much use for finding out the direction of change in a chemical or physical process. We want a more general and mathematical formulation which was supplied by Clausius.

Clausius shifted the interest from the problem of convertibility of heat to work, to that of change of thermal state of the working substance, for it is only the working substance which undergoes a thermodynamical change in the process. He observed that when the heat Q is added to it reversibly at temperature T, and Q' taken away from it reversibly at temperature T' we have[1]

$$\frac{Q}{T} - \frac{Q'}{T'} = 0. \qquad . \quad . \quad . \quad . \quad . \qquad (11)$$

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[1] If we regard Q as an algebraic symbol, positive for heat absorbed and negative for heat rejected, then (11) becomes $\Sigma Q/T = 0$. Any reversible transformation can be supposed to be made up of a number of infinitesimal reversible isothermal and adiabatic processes as shown in Fig. 1, and therefore for any *reversible* cyclic process such as ABCDA or any other, it can be proved in the manner shown in the text that $\oint \delta Q/T = 0$, which is known as Clausius' theorem. For irreversible processes, as for example those accompanied by ordinary thermal conduction along AB and CD, it readily follows from Carnot's theorem that if T represents the temperature of the source which surrenders heat to the working substance, we must have $\oint \delta Q/T < 0$, for

$$\frac{Q - Q'}{Q} < 1 - \frac{T'}{T}, \quad \text{or} \quad \frac{Q'}{T'} > \frac{Q}{T}.$$

This property was utilised in defining an additional thermodynamic function (Entropy) for the gas which proved to be of great importance in the further development of thermodynamics. In the following deduction, we have followed Ewing's treatment.[1]

Let us take a gas in a definite state A (Fig. 1), and compare this state with another state B, which is obtained by the addition of heat energy. It is easy to see that the amount of heat added from outside may be anything, owing to the variety of ways in which heat can be added. This can be visualised by drawing curves between A and B. There may be an infinite number of curves passing between A and B, corresponding to the infinite number of ways in which heat can be added. It will now be shown that the integral

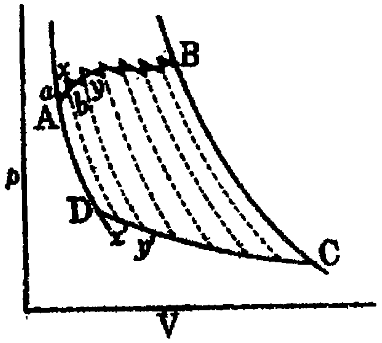

Fig. 1.—The entropy function.

$$\int_A^B \frac{\delta Q}{T}$$

measured along any reversible process does not depend on the path, but only on the coordinates of A and B.

Let us draw two adiabatics through A and B, and draw an isothermal DC at temperature t cutting these adiabatics in D and C respectively. Let us now divide the area ABCD into a number of elementary Carnot cycles $xyy'x'$ as in Fig. 1 (xy, $x'y'$, isothermals, and xx', yy' adiabatics).

Let δQ be the amount of heat absorbed at temperature T while the point shifts from x to y and δq be the amount given up while it shifts from y' to x'. Then we have

$$\frac{\delta Q}{T} = \frac{\delta q}{t}.$$

Adding up for all the Carnot cycles between A and B, we have

$$\Sigma \frac{\delta Q}{T} = \Sigma \frac{\delta q}{t} = \frac{1}{t} \Sigma \delta q. \quad . \quad . \quad . \quad . \quad (12)$$

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[1] See Glazebrook, *A Dictionary of Applied Physics*, Vol. I, p. 271.

This is the value of $\int \delta Q/T$, along the zigzag path $Aabxy\ldots B$, for the value of the integral along the adiabatics Aa, bx, ... is 0.

In the limiting case when the Carnot cycles are infinitely small the zigzag path $Aabxy\ldots B$ coincides with AB. Hence

$$\int_A^B \frac{\delta Q}{T} = \sum \frac{\delta Q}{T} = \frac{1}{t}\,\Sigma\,\delta q. \quad . \quad . \quad . \quad . \quad (13)$$

The value of the integral $\int_A^B \frac{\delta Q}{T}$ is now seen to be equal to $\Sigma\,\delta q/t$, and hence it is independent of the path between A and B.

Instead of taking the particular isothermal DC we may draw any other isothermal t' cutting AD and BC, the value of the integral cannot be thereby changed, for if we construct a number of Carnot cycles between the first and the second isothermal we have

$$\frac{1}{t}\,\Sigma\,\delta q = \frac{1}{t'}\,\Sigma\,\delta q'.$$

The points A and B may be taken anywhere on the adiabatics AD and BC respectively, the value of the integral will remain the same, for $\int \delta Q/T$ along an adiabatic is zero since $\delta Q = 0$. Hence it follows that if we pass from one adiabatic to another the expression $\int_1^2 \frac{\delta Q}{T}$ denotes a quantity which increases by a definite amount independent of the manner of transformation. For the state 1 we may take any standard state n. Then the value of the integral $\int_n^A \frac{\delta Q}{T}$ along any reversible path, depends only on the states n and A as proved above. Now since the state n is fixed, the value of this integral will be a function of the state A only and can be written as s_A. The quantity s_A is called the *entropy* of the substance in the state A. The entropy thus defined requires the arbitrary choice of the standard state n and would have a different value if we chose a different standard state, the difference between these two values being the entropy of the old standard state with respect to the new. Thus the entropy becomes indeterminate to the extent of an additive constant which represents the entropy of the arbitrarily chosen standard state with respect to the state where the entropy is zero. We can thus write

$$s_A = s_n + \int_n^A \frac{\delta Q}{T}, \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

where s_n denotes the entropy of the substance in the state n. This is the thermodynamic definition of entropy. As far as the first and the second laws of thermodynamics are concerned, this constant s_n cannot be determined and the absolute value[1] of the entropy cannot be found. Generally we are concerned only with changes in entropy and hence we can meas[illegible] from any arbitrary zero (cf. p. 247 for steam, where the entropy of water at 0°C is put as zero) as the entropy of the assumed standard state will cancel out in taking the difference.

From (14) we see that the entropy s in any state represented by T, v is given by

$$s - s_0 = \int_{T_0,\, v_0}^{T,\, v} \frac{\delta Q}{T}, \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

where s_0 denotes the entropy at T_0, v_0, and δQ is measured along a reversible process. Thus to measure the entropy in any state we have to take the substance along any reversible process arbitrarily chosen, to its standard state and find the value of $\int \delta Q/T$ along this path. The entropy though conveniently measured with respect to a reversible process, exists quite independently of it. Further, it will be observed that this definition enables us to measure entropy of equilibrium states only; entropy of non-equilibrium states cannot be measured in this manner as we cannot connect non-equilibrium state to the standard state by a reversible process. Nevertheless it is evident that the entropy of a system not in equilibrium, will be smaller than that of the resulting equilibrium state as the latter can be obtained from the former by an irreversible process, in which entropy increases.

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[1] This is partly rendered possible by the third law of thermodynamics according to which the entropy of each element in the perfect crystalline state at the absolute zero, may be assumed to be zero (Planck's enunciation). This assumption, however, need not be true; it is, in fact, almost a hopeless task to fix the zero of entropy. For further discussion see Chaps. IX and XVII.

The above treatment is perfectly general and will hold whatever substance is taken as the working substance. Now, if the work done is by expanding against an external pressure we have from the first law for any process, reversible or irreversible, $\delta Q = du + pdv$, where p stands for the external pressure at every stage of the process. But in equation (15) we have to substitute the value of δQ along a reversible process. Now the process represented by equation (11) of Chap. V embodying the first law, is reversible only when the external pressure p is always equal to the intrinsic pressure of the substance, *i.e.*, when the process is quasi-static and non-dissipative. Hence we get

$$s_T - s_0 = \int_{T_0,v_0}^{T,v} \frac{du+pdv}{T}, \quad . \quad . \quad . \quad . \quad (15a)$$

where p denotes the equilibrium pressure of the substance at every stage of the process.

It is easily seen that entropy is proportional to the mass of the substance taken for if we take M grams of the substance $dU = Mdu$, $dV = Mdv$ and hence $S = Ms$.

6·5. The Integrating Factor.—From the foregoing discussion we have seen that the expression $\int_1^2 du+pdv$ cannot be evaluated in terms of the thermodynamical quantities representing the states 1 and 2; a knowledge of the path of transformation is also necessary. On the other hand equation (15a) shows that the quantity $\int_1^2 \frac{du+pdv}{T}$ can be completely represented in terms of the thermodynamical coordinates defining the initial and final states and may be written as $s_2 - s_1$. For an infinitesimal reversible process (15) yields

$$ds = \frac{\delta Q}{T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Thus we see that, though δQ or $du + pdv$ is not a perfect differential, $\delta Q/T$ or $(du+pdv)/T$ is a *perfect differential* (ds), since it is the differential of an actual function s of the two variables of state. Thus $1/T$ is the integrating factor to the differential expression $du+pdv$.

The following example will give an idea to the student, who is not a skilled mathematician, of what is meant by the term integrating factor. Let us take the differential expression $\delta w = 3xydx + 2x^2dy$. We have

$$\frac{\partial w}{\partial x} = 3xy;\ \frac{\partial w}{\partial y} = 2x^2.$$

$$\frac{\partial^2 w}{\partial y \partial x} = 3x;\ \frac{\partial^2 w}{\partial x \partial y} = 4x,$$

$$\therefore \frac{\partial^2 w}{\partial y \partial x} \neq \frac{\partial^2 w}{\partial x \partial y}. \qquad \ldots \qquad (17)$$

It can be easily verified that the function $\delta w = 3xydx + 2x^2dy$, cannot be integrated. In fact, it can be shown from calculus that the condition for integrability is just the reverse of (17). If however δw is multiplied by xy, the resulting function $3x^2y^2dx + 2x^3ydy = d(x^3y^2)$, is integrable and the quantity xy is called the integrating factor of the differential expression δw.

In the foregoing discussion we have adopted the conventional historical method initiated by Carnot and elaborated by Kelvin and Clausius for the mathematical formulation of the Second Law in the form $dQ = Tds$. Using an ideal Carnot engine and making use of the Second Law in the form 'Impossibility of perpetual motion of the second kind' Carnot's theorem regarding efficiency of engines was deduced and absolute temperature T defined. Then Clausius theorem was proved and the entropy function inferred showing that $1/T$ is the integrating factor to the function $du + pdv$. From a mathematical point of view this procedure is unsatisfactory and an axiomatic treatment is called for which was supplied by Carathéodory[1] in 1909. Carathéodory's principle, which is his mathematical statement of the second law, states :

In the neighbourhood of any arbitrary initial state of a physical system, there exist neighbouring states as close as we please to the initial state, which are not accessible from the initial state along adiabatic paths.

Starting from this principle and making use of a mathematical theorem, Carathéodory inferred, without the aid of Carnot engines and refrigerators, the existence of the entropy function and an integrating factor connected with the Kelvin temperature T. The simplest integrating factor is $1/T$, and the corresponding complete differential is $ds = dQ/T$. For detailed exposition, the original papers may be consulted.

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[1] *Math. Ann.*, **67**, 355, 1909. See also Born, *Phys. Zeits.*, **20**, pp. 218, 249, 282, 1921; Buchdahl, *Amer. Jour. Phys.* (1949). For a good account in English see Bronsted, *Principles and Problems in Energetics*, pp. 40—50 (1955).

6·6. Entropy of a System.—In §6·4 it was shown that if the entropy per unit mass of a substance is s, the entropy of m grams of the substance is ms. It can be shown in a similar way that if we have a system of bodies in *thermodynamical equilibrium* their masses being $m_1, m_2 \ldots$ and specific entropies $s_1, s_2, \ldots$, the entropy of the whole system is

$$S = m_1 s_1 + m_2 s_2 + \ldots \quad . \quad . \quad . \quad (18)$$

6·7. Entropy of the Universe Remains Constant in Reversible Processes.—If during any reversible process the heat δQ enters the system from the surroundings at the temperature T, the increase in entropy of the system is $\delta Q/T$ and that of the local surroundings $-\delta Q/T$, the total change in entropy, which we may call the entropy change of the universe due to the process, is zero.

Considering the Carnot cycle, we notice that the working substance has the same entropy at the end of the cycle as at the beginning since it returns to the same state. The loss in entropy of the source is Q_1/T_1, the gain by the condenser is Q_2/T_2 and hence the net gain in the entropy of the universe is

$$\frac{Q_2}{T_2} - \frac{Q_1}{T_1} = 0.$$

Thus the entropy of the universe remains unaltered by this process.

In the *isothermal expansion* of the working substance in the first part of the Carnot cycle the increase in entropy of the working substance is Q_1/T_1, the loss by the source is Q_1/T_1 and hence the total entropy remains constant.

From Eqn. (18) we see that the increase in entropy of a gram-molecule of perfect gas in isothermal reversible expansion from volume V_1 to V_2 at temperature T is

$$\Delta S = \int_{V_1}^{V_2} \frac{dU + pdV}{T} = \frac{1}{T}\int_{V_1}^{V_2} p\, dV = \mathrm{R}\, ln \frac{V_2}{V_1} \quad . \quad . \quad . \quad (19)$$

The change in entropy during a *reversible adiabatic compression or expansion* is zero. For in such a process the change in entropy is $\Delta S = \int (dU + pdV)/T$, but by the condition of the process $dU + pdV = 0$, from the first law, hence $\Delta S = 0$ *i.e.*, the *entropy* remains constant in a reversible adiabatic process. Adiabatic curves are, therefore, sometimes known as "*Isentropics*".

6·8. Entropy Increases in Irreversible Processes.— It will now be shown that entropy of the universe increases as a result of irreversible processes. Irreversible processes are of various types, some of which have already been considered in Chap. IV. We shall enumerate here a few typical irreversible processes: (1) Processes which exhibit external mechanical irreversibility such as the irregular stirring of viscous liquid, the development of heat by friction, the flow of electricity through a resistor, etc. (2) Processes which exhibit internal mechanical irreversibility such as the rushing of an ideal gas into a vacuum (free expansion), Joule-Thomson expansion (Chap. XII); (3) Processes exhibiting thermal irreversibility such as conduction or radiation of heat from the system to the surroundings or between the different parts of the system itself; (4) Processes exhibiting chemical irreversibility such as mixing of two liquids or diffusion of two inert ideal gases, etc. We shall prove here the theorem of increase of entropy for a few processes only.

(*i*) *Increase of Entropy during Conduction or Radiation of Heat.*— Suppose a small quantity of heat δQ, is conducted away from a body A at temperature T_1 to another body B at temperature T_2 $(T_1>T_2)$, and let δQ be so small that the temperatures T_1 and T_2 of the bodies are not appreciably altered in the process, then A loses entropy equal to $\delta Q/T_1$ while B gains entropy by an amount $\delta Q/T_2$. Thus the total gain in entropy of the two bodies is

$$\Delta S = \delta Q\left(\frac{1}{T_2}-\frac{1}{T_1}\right), \quad . \quad . \quad . \quad (20)$$

which is positive since $T_1>T_2$. Hence the entropy of the universe increases as a result of thermal conduction. Similarly in the case of radiation, if a quantity of heat δQ is radiated from the body A to the body B, the gain in entropy is given by the same expression. Thus increase of entropy is always produced by the equalisation of temperature.

(*ii*) *Gas rushing into a vacuum.*—Consider a perfect gas in a vessel rushing into an evacuated vessel and let the whole system be thermally insulated. Since the gas is perfect, the temperature does not change in the process. The gain in entropy may be calculated by finding the value of $\int\delta Q/T$, along any reversible path connecting the initial and final states but not along the original irreversible path. The reversible process, most convenient for this purpose is an isothermal quasi-static expansion of the gas from the initial volume to the final volume. From (19) the increase in entropy will therefore be given by

$$\triangle S = \frac{1}{T}\int p dV = \mathrm{R}\, ln\, \frac{V_2}{V_1}, \quad . \quad . \quad . \quad (21)$$

where V_1, V_2 denote the initial and final volumes of the gas. Hence the entropy of the system increases in this irreversible process.

The student should try to prove for himself that increase of entropy occurs in other irreversible processes also.

6·9. The Entropy of a Perfect Gas.—Let us take m grams of a perfect gas having the temperature T and occupying the volume $\mathbf{V}$. The entropy from (15*a*) is given by

$$ms = \int \frac{d\mathbf{U}+pd\mathbf{V}}{T} + \text{constant},$$

where the integral sign denotes an indefinite integral. Since $d\mathbf{U} = mc_v dT, p = m\mathrm{R}T/M\mathbf{V}$, we have

$$ms = m\left(c_v \frac{dT}{T} + \frac{\mathrm{R}}{M}\, ln \mathbf{V}\right) + \text{const.}$$

If c_v is independent of T, as is the case with monatomic gases but not polyatomic gases, this equation becomes

$$ms = m\left(c_v\, ln\, T + \frac{\mathrm{R}}{M}\, ln\, \mathbf{V}\right) + \text{const.} \quad . \quad . \quad (22)$$

We can also express ms in terms of pressure. Using the relation $c_p = c_v + \mathrm{R}/M$, equation (22) yields

$$ms = m\,(c_p\, ln\, T - \frac{\mathrm{R}}{M}\, ln\, p) + \text{const.}, \quad . \quad . \quad (23)$$

this constant being different from that in (22).

These two expressions give us entropy completely as far as variations in the value of the thermodynamical coordinates are concerned. But the constant has to be carefully defined.

It is easy to see that the constant is proportional to the mass in equation (23), but not in (22). For if we take a mass of gas and divide it into two equal halves by sliding a partition between them, no work is done and hence the total entropy of the system remains the same as before, and the entropy of each half of the gas is just equal to half the previous expression for entropy given by equation (23). But the values of p and T in this equation remain unaltered, hence the constant must become halved for this half of the gas. We can therefore put the constant equal to mc and write

$$ms = m\left(c_p\, ln\, T - \frac{R}{M}\, ln\, p + c\right). \quad . \quad . \quad . \quad (24)$$

Let us express (24) in terms of the molar specific heat. Then

$$ms = \frac{m}{M}(C_p\, ln\, T - R\, ln\, p + R\, ln\, i), \quad . \quad . \quad . \quad (25)$$

where we have put $Mc = R\, ln\, i$ merely to preserve symmetry in the expression. The constant 'i' is independent of T, p and also of the number of molecules but is characteristic of the molecule. It cannot be obtained from classical ideas, but in Chaps. XI and XVII we shall see how the quantum theory enables us to evaluate it in terms of the constants of the molecule of which the gas is composed.

Equation (25) can now be expressed in terms of the volume. We have

$$ms = \frac{m}{M}\left(C_v\, ln T - R\, ln\, n + R\, ln \frac{i}{k}\right), \quad . \quad . \quad . \quad (26)$$

where n denotes the number of molecules per unit volume. The second term containing n thus involves the volume.

Exercise 1. Calculate the change in entropy of the universe occurring when 10 grams of water at 60°C are mixed adiabatically with 30 gm. of water at 20°C.

Exercise 2. Calculate the increase in entropy of two grams of oxygen when its temperature is raised from 0°C. to 100°C. and its volume is also doubled.

$$\Delta S = 2 \times 2{\cdot}3026 \left[\frac{5{\cdot}035}{32} \log \frac{373}{273} + \frac{1{\cdot}986}{32} \log 2\right] = 0{\cdot}85 \frac{\text{cal.}}{\text{degree}}.$$

6·10. Entropy of a Mixture of Gases.—Suppose we have a mixture of gases of different species occupying the total volume V; let λ_1, λ_2. . ., denote the number of mols of the different species in the total volume. The partial pressures are

$$p_1 = \frac{\lambda_1 RT}{V},\ p_2 = \frac{\lambda_2 RT}{V}, \ldots$$

and the total pressure $p = \dfrac{(\Sigma \lambda_r)\, RT}{V} = \dfrac{\lambda RT}{V}$.

Let us put $x_1 = \dfrac{\lambda_1}{\lambda},\ x_2 = \dfrac{\lambda_2}{\lambda},\ . \ . \ . \ . \ .$

where x_1, x_2. . ., denote the concentrations of the individual type of molecules. Then

$$p_1 = x_1 p,\ \ p_2 = x_2 p,\ \ldots .$$

What will be the entropy of this mixture? W. Gibbs showed that it will be given by

$$S = \Sigma \lambda_r (C_p \ln T - R \ln px + R \ln i)_r \quad . \quad . \ (27)$$

i.e., we have to use the partial pressure in place of '*p*' in the expression (25), and take the sum of the entropies of the different species. This theorem was proved in the following way :—

Let us take two gases (1) and (2), originally contained in the volume AA′ (Fig. 2) and suppose their partial pressures are p_1 and p_2. Let us now try to separate the gases by means of semipermeable membranes[1]. For this purpose we imagine a hollow cylinder BB′ of the same volume as AA′ , and capable of sliding freely without friction through AA′ which is fixed. Let us further assume that B′ is permeable to gas (1), while A′ is permeable to gas (2) only, A and B are non-permeable to both[2]. At the start B′ is in contact with A, and B with A′. Now let BB′ move upwards very slowly. We have now only gas (1) in AB′, gases (1) and (2) in A′B′, and gas (2) in A′B.

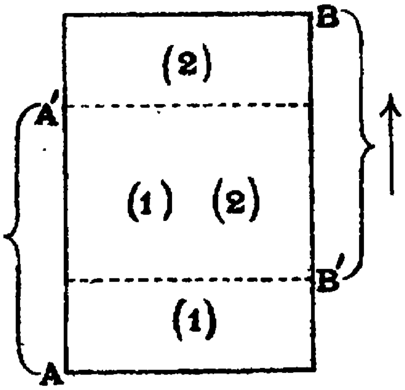

Fig. 2.—Separation of two gases by semipermeable membranes.

In the steady state membrane equilibrium exists when the pressure of (1) is the same on both sides of B′. Thus B′ is only subjected to pressure by (2) downwards. Similarly B is also subjected to the pressure of the gas (2) upwards. Since these pressures are identical (partial pressure of 2), BB′ is as a whole subjected to no pressure, and if it is moved infinitely slowly, so that at every instant there is membrane equilibrium, then no work is done in moving BB′ and hence if the process is carried on at constant temperature it will not exchange heat with the surroundings, since the internal energy U of a perfect gas is independent of the volume. Thus the separation has been carried out by a reversible isothermal process. Hence from the Second Law, the entropy remains unchanged in the process. When B′ comes to A′, the two gases have entirely separated, and can be considered separately. Therefore the entropy of the mixture before separation, is equal to the sum of the entropies of the gases after separation. The latter is given by equation (27). Hence the entropy of the mixture will be given by (27).

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[1] As an example of semi-permeable membranes, we may take a tube of palladium. If it is heated, it becomes permeable to H_2 gas, and allows this to pass but is not permeable to oxygen. These tubes are now very largely used for the introduction of H_2 into discharge tubes. A tube is sealed to a vacuum tube; if the tube is now heated by a Bunsen burner, the free hydrogen from flame gases passes into the tube and can be recognised by its spectrum.

[2] It is true that perfect semi-permeable membranes of the type contemplated here do not actually exist for any gas whatsoever because no membrane could be absolutely impermeable to any gas. Still the arguments would remain valid, if the quantity of gas passing through the membrane is so small as to be negligible. We shall further suppose that there exists a special membrane, permeable to every gas with which we deal. Whether this is actually so is of no importance.

6·11. Increase in Entropy due to Diffusion of two Gases into one another.—Suppose the two gases were initially at the pressure p, the temperature T and therefore occupying the volumes Vx_1, Vx_2 where x_1, x_2 are fractions and $x_1+x_2=1$. Let the common boundary be now taken off so that the gases diffuse into each other, and we get a homogeneous mixture with the pressure p, volume V and temperature T. We can show that an increment in entropy has taken place in this process.

The entropy of the system before mixture is

$$S = \lambda_1 (C_p \ln T - R \ln p + R \ln i)_1 + \lambda_2 (C_p \ln T - R \ln p + R \ln i)_2.$$

The partial pressures of the two gases in the mixture will be px_1 and px_2. Hence from (27) the entropy of the mixture is

$$\lambda_1 (C_p \ln T - R \ln px_1 + R \ln i)_1 + \lambda_2 (C_p \ln T - R \ln px_2 + R \ln i)_2.$$

Hence the increase in entropy

$$\Delta S = -R(\lambda_1 \ln x_1 + \lambda_2 \ln x_2). \quad . \quad . \quad . \quad . \qquad (28)$$

Since x_1 and x_2 are fractions, the expression is positive, *i.e.*, there is an increment of entropy when the two gases diffuse into each other. In the general case, when a number of gases occupying the volumes Vx_1, Vx_2 diffuse into each other, the total change in entropy

$$\Delta S = -R \sum \lambda \ln x. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (29)$$

It may be remarked that equation (28) holds for two different gases but not for two identical gases[1]. If we were to apply it to two portions of the same gas, it would show an increase of entropy when two identical gases at the same pressure and temperature are put into communication, but obviously it cannot be so and there can be no increase in entropy in this special case. This is called Gibbs' paradox and the real cause of this failure can be given from quantum mechanics. The molecules being identical there is nothing to distinguish the state after diffusion from the initial state.

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[1] Equation (28) holds even for statistically different molecules, *i.e.*, rotational isomers such as ortho- and para-hydrogen.

6·12. Principle of Increase of Entropy.—In the foregoing section we have shown for a few irreversible processes that increase of entropy takes place during such a process. We might consider other irreversible processes and show in each case that increase of entropy takes place. This result is quite general and may be stated as follows :—*The entropy of a system of bodies tends to increase in all physical and chemical processes occurring in nature, if we include in the system all such bodies which are affected by the change.* In the limiting case of a reversible process the entropy remains constant. This is the *principle of increase of entropy*[1] which may be established for any general case by making use of any one of the previous formulations of the second law of thermodynamics.

6·13. Second Law of Thermodynamics.—We may call this principle of increase of entropy itself as the second law of thermodynamics. In fact Clausius summed up the first law by saying that the *energy of the world remains constant* and the second law by saying that the *entropy of the world tends to a maximum.*

A more formal statement of the second law of thermodynamics can now be made in terms of the properties of the system itself without reference to any process. This involves the following two statements :—

(a) For any system a characteristic thermodynamical function called entropy may be defined which is such that the difference of entropies between two states (1) and (2) is given by $\int_1^2 \delta Q/T$ where the integral is to be taken over any reversible path connecting the two states, and which is a variable of state.

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[1] For a general discussion of the second law and the principle of increase of entropy see Hausen, *Phys. Zeits.*, **35**, 517, 1934.

(b) The entropy of a closed system (*i.e.*, one that has no interaction of any sort with the surroundings and thus has constant energy) can never decrease.

6·14. Supposed Violation of the Second Law.—Maxwell invented an ingenious contrivance which violated the Second Law as enunciated above. Following Boltzmann's idea (§6·2), he imagined a super-human being which could discriminate between the individual molecules. Suppose such a creature, usually known as *Maxwell's demon*, stands at the gate in a partition separating two volumes of the same gas at the same temperature and pressure and, by opening and shutting the gates at the proper moment, allows only the faster moving molecules to enter one enclosure and the slower molecules to enter the other enclosure. The result will be that the gas in one enclosure will be at a higher temperature than in the other and the entropy of the whole system decreases though no work has been done. This apparently violates the Second Law.

We observe however that to Maxwell's demon the gas does not appear as a homogeneous mass but as a system composed of discrete molecules. The law of entropy does not hold for individual molecules, but is *a statistical law* and is valid only when we are compelled to deal with matter in bulk, and are unable to direct or control the motion of individual molecules. Further we shall see in Chap. IX that this law is of the nature of a law of probability and asserts that it is highly probable that the entropy of a closed system increases but there is always a chance, though a very meagre one, that the entropy may decrease..

6·15. Entropy and Unavailable Energy.—Consider a source at temperature T_1 and suppose it yields a quantity of heat Q to a working substance. If the lowest available temperature for the condenser of the Carnot cycle is T_0, the amount of heat rejected is $Q\ T_0/T$, and the available energy is $Q(1-T_0/T)$. Now suppose a quantity of heat Q passes by conduction from a body at temperature T_2 to another at temperature T_3 the gain in unavailable energy is $Q\left(\frac{1}{T_3}-\frac{1}{T_2}\right)T_0$, T_0 being the lowest available temperature. Hence the increase of unavailable energy is equal to the increase of entropy multiplied by the lowest temperature available. Thus entropy is a measure of the unavailability of energy, and the law of entropy implies that the available energy in the world tends to zero. This is also known as the principle of degradation or 'running downhill' of energy.

6·16. Physical Concept of Entropy.—The entropy of a substance is a real physical quantity defined by equation (14) or (16) and can be easily evaluated for a solid or a perfect gas (§6·9) except for an additive constant representing the entropy at the absolute zero. We also saw that entropy remains constant when the substance undergoes a reversible adiabatic compression or expansion. Further entropy was shown to be a definite single-valued function of the thermodynamical coordinates defining the state of the body like the temperature, pressure, volume, internal energy, state of magnetisation, etc. It is difficult to form a tangible conception of entropy because there is nothing physical to represent it; it cannot be felt like temperature or pressure. We can however readily infer that it is a measure of the *disorder* or randomness in the molecular arrangement of the system. We have seen that addition of heat to a system increases its entropy; from the kinetic point of view addition of heat produces a more violent agitation of the molecules. Thus by the continuous abstraction of heat the entropy of the system decreases and the molecular motion tends to vanish and the molecular arrangement attains a state of great order. Hence increase of entropy implies a transition from an ordered to a less ordered state of affairs.

It will be shown in Chap. IX that entropy is a function of the *probability* of that macroscopic state, probability being maximum for maximum disorder. Thus growth of entropy implies a transition from a more to a less available energy, from a less probable to a more probable state, from an ordered to a less ordered state of affairs. The idea of entropy is necessitated by the existence of irreversible processes. It is measured in calorie per degree or erg per degree.

PROBLEMS

1. Two gram-molecules of hydrogen perform a free expansion from a volume of 10 litres to a volume of 30 litres, the temperature being 25°C. What is the entropy change of the Universe? What would be the change in entropy of the gas if the expansion were performed reversibly and isothermally?

2. Calculate the change in entropy of the universe when a current of 5 amperes flows for 10 sec. through a thermally insulated resistance of 10 ohms, initially at a temperature of 20°C, given that the resistor has a mass of 10 gm. and $c_p = 0 \cdot 2$ cal./gm. deg.

3. Calculate the change in entropy when one gram-molecule of oxygen at the atmospheric pressure diffuses into 4 gram-molecules

of nitrogen at the same pressure, the final pressure being the atmospheric pressure.

4. Prove that for any substance

$$s(T_1, p) = \int_{T_0}^{T_1} \frac{c_p\, dT}{T} + S(T_0, p),$$

$$s(T_1, v) = \int_{T_0}^{T_1} \frac{c_v\, dT}{T} + S(T_0, v).$$

BOOKS RECOMMENDED

1. Same as mentioned in Chap. V.
2. *Handbuch der Physik* Vol. 9. Chap. 1.
3. For application of relativistic ideas to Thermodynamics, see Tolman, *Relativity, Thermodynamics and Cosmology* (1934) Chaps. V and IX (Clarendon Press, Oxford).
4. J. N. Bronsted, *Principles and Problems in Energetics* (1955), Interscience Publishers, Inc. New York.

CHAPTER VII

GENERAL THERMODYNAMICAL THEOREMS

7·1. The Thermodynamical Relationships (Maxwell). —With the aid of the knowledge that the entropy-function is uniquely determined by the thermodynamical coordinates of the state, or in other words, ds is a perfect differential, we shall prove a few general thermodynamical theorems applicable to a simple homogeneous system (gas, liquid or solid) consisting of a single chemical substance.

We have from the first law $\delta Q = du + pdv$, and from the second law $\delta Q = Tds$[1] where δQ is the heat taken in a reversible process. Combining these we get

$$Tds = du + pdv, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where p is the equilibrium pressure, *i.e.*, the pressure of the substance as given by its equation of state. Hence[2]

$$du = Tds - pdv. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now if x and y are any two independent variables we have, since du is a perfect differential,

$$\frac{\partial^2 u}{\partial x \partial y} = \frac{\partial^2 u}{\partial y \partial x}.$$

From this relationship, by substitution from (2) and remembering that ds and dv are also perfect differentials, it can be shown that

$$\frac{\partial(T,s)}{\partial(x,y)} = \frac{\partial(p,v)}{\partial(x,y)}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\frac{\partial(T,s)}{\partial(x,y)}$ stands for the Jacobian $\begin{vmatrix} \frac{\partial T}{\partial x} & \frac{\partial T}{\partial y} \\ \frac{\partial s}{\partial x} & \frac{\partial s}{\partial y} \end{vmatrix}$

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[1] This result was deduced on p. 311 from the second law. In this form the second law has found many important applications. The experimental confirmation of the results deduced in the following pages is a direct proof of the second law.

[2] Equation (2) is valid for all changes taking place in a system. If the change is reversible, Tds is equal to the heat applied to the system and pdv is equal to the work done by it. If the change is irreversible, the heat applied is less than Tds and the work done by it also is less than pdv, but still $du = \delta Q - \delta W$ as required by the first law.

Any two of the four quantities T, s, p, v can be chosen as the independent variables x, y. This can be done in six different ways, and correspondingly, we have six thermodynamical relationships, though all of them are not independent.

7·2. First Relation.—Let us take the temperature and the volume as independent variables, and put $x = T$, $y = v$ in (3). Then

$$\frac{\partial T}{\partial x} = 1, \; \frac{\partial v}{\partial y} = 1,$$

and

$$\frac{\partial T}{\partial y} = \frac{\partial T}{\partial v} = 0, \; \frac{\partial v}{\partial x} = 0,$$

since T and v are independent. Hence we have

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which implies that the increase of entropy per unit increase of volume at constant temperature is equal to the increase of pressure per unit increase of temperature when the volume is kept constant. We can apply equation (4) to the equilibrium between two states of the same substance. Multiplying both sides by T,

$$\left(\frac{\delta Q}{\delta v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which means that the latent heat of isothermal expansion is equal to the product of the absolute temperature and the rate of increase of pressure with temperature at constant volume. Thus if a body changes its phase at $T°$ and absorbs the latent heat L, and the specific volumes in the first and the second phases are v_1 and v_2, equation (5) yields

$$\frac{L}{v_2 - v_1} = T\left(\frac{\partial p}{\partial T}\right)_v .$$

When we apply this equation to change of phase such as the vaporization of liquid, the various thermodynamic quantities refer to a mixture of the liquid and vapour in equilibrium. For such a case, it is evident that

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial p}{\partial T}\right)_{\text{sat}}.$$

since the pressure is saturation pressure and is consequently independent of v, being only a function of T. Hence

$$\left(\frac{\partial p}{\partial T}\right)_{\text{sat}} = \frac{L}{T(v_2 - v_1)} \cdot \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This is Clapeyron's equation and is one of the most important formulae in thermodynamics. Alternative proofs, somewhat more rigorous and instructive, will be given in Chap. VIII.

Let us first employ (6) to find the change in the freezing point of a substance by pressure. In the case of water at 0°C.

$L = 79{\cdot}6 \times 4{\cdot}186 \times 10^7$ ergs per gram (latent heat of fusion)

$T = 273{\cdot}16$

$v_2 = 1{\cdot}0001$ c.c. (specific volume of water at 0°C).

$v_1 = 1{\cdot}0908$ c.c. (specific volume of ice at 0°C.)

$$\therefore \frac{dp}{dT} = \frac{79{\cdot}6 \times 4{\cdot}186 \times 10^7}{273{\cdot}16 \times (1{\cdot}0001 - 1{\cdot}0908)}.$$

Now if $\delta p = 1$ atmosphere $= 1{\cdot}013 \times 10^6$ dynes,

$$\delta T = -0{\cdot}0075°\text{C}.$$

This shows that the melting point of ice is lowered by increase of pressure, the lowering per atmosphere being 0·0075°. The pressure necessary to lower the melting point by 1°C. is 1/0·0075 = 133 atmos. These results were quantitatively verified by Kelvin. His experimental results are given in Table 1.

Table 1.—Depression of freezing point with increase of pressure.

Increase of Pressure	Depression of freezing point in °C.	
	observed	calculated
8·1 atmos. ..	0·0580	0·0607
16·8 „ ..	0·1289	0·1260

For substances which contract on solidification the melting point will be increased by pressure. Thus for acetic acid whose melting point is 16·5°C., de Visser found experimentally that an increase of pressure by 1 atmosphere increases the melting point by 0·02432°C. while equation (6) gave 0·02421°C. This verifies relation (6). The same equation may also be employed to calculate the latent heat. For the vaporization of water at 100°C., we have the following data :—

$$T = 373\cdot 2,\ v_1 = 1 \text{ c.c.},\ v_2 = 1674 \text{ c.c.}$$
$$dp/dT = 27\cdot 12 \text{ mm. of mercury.}$$
$$\therefore L = \frac{373\cdot 2 \times (1674-1) \times 27\cdot 12 \times 1\cdot 013 \times 10^6}{760 \times 4\cdot 186 \times 10^7} = 539 \text{ cal.}$$

The accurate experiments of Henning give $L = 538\cdot 7$ cal. at 100°C. which is very close to the calculated value.

Application to a liquid film.—Equation (4) may also be applied to the case of a liquid film. If such a film is stretched, its total volume remaining constant, the energy equation[1] for this case is

$$(\delta Q)_v = du - 2\mathcal{T} dA,$$

for the work done by the film is $-2\mathcal{T} dA$ where $\mathcal{T}$ is the surface tension and dA the increase in area of the film. The usual term pdv on the right has disappeared since the total volume remains constant. Hence corresponding to p and dv we have in this case $-2\mathcal{T}$ and dA respectively. Hence equation (5) yields

$$\left(\frac{\delta Q}{\delta A}\right)_{T,v} = -2T\left(\frac{\partial \mathcal{T}}{\partial T}\right)_{v,A}$$

and for a finite change,

$$\delta Q = -2T\left(\frac{\partial \mathcal{T}}{\partial T}\right)_{v,} dA.$$

For a liquid the surface tension decreases with temperature, therefore $\partial\mathcal{T}/\partial T$ is negative and ∂Q is positive. Hence an amount of heat ∂Q must be supplied to the film when it is stretched in order that its temperature may remain constant. In an adiabatic stretching the temperature will fall by an amount

$$\delta T = \frac{2T}{C_A}\left(\frac{\partial \mathcal{T}}{\partial T}\right)_{v,A} dA,$$

where C_A is the heat capacity of the film.

7·3. Second Relation.—Another important application of the thermodynamic formulae consists in their application to certain adiabatic changes, such as the sudden compression of a liquid, or sudden stretching of a rod. For this case let us put $x = T$, $y = p$.

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[1] We may write this equation in the form $du - 2\mathcal{T} dA = Tds$ and treat this equation as we treated equation (1) in §7·1.

Equation (3) then reduces to

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \quad . \quad . \quad . \quad (7)$$

which means that the decrease of entropy per unit increase of pressure during an isothermal transformation is equal to the increase of volume per unit increase of temperature when the pressure is kept constant. Multiplying both sides by T we have

$$\left(\frac{\delta Q}{\delta p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p = -Tv\alpha,. \quad . \quad . \quad . \quad (8)$$

where α is the coefficient of volume expansion at constant pressure.

From this relation it follows that if α is positive, *i.e.*, the substance expands on heating, $(\delta Q/\delta p)_T$ is negative, and hence in this case an amount of heat must be taken away from the substance when the pressure is increased, in order that the temperature may remain constant. That is, heat is generated when a substance which expands on heating is compressed. For substances which contract on heating, a cooling should take place.

These conclusions were verified experimentally by Joule who worked with fish-oil and water. The liquid was contained in a vessel closed at the top by a piston, and the pressure was suddenly increased by placing weights upon the piston. The change in temperature was measured by a thermopile. Assuming the process to approximate to a reversible adiabatic increase of pressure, we can use equation (8) to calculate the increase in temperature $\triangle T$ produced by a sudden increase of pressure $\triangle p$. We have[1]

$$dT = \frac{\delta Q}{c_p} = \frac{Tv\alpha}{c_p}dp, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where c_p is the specific heat of the substance and v its specific volume. Or

$$\triangle T = \int\frac{Tv\alpha}{c_p}dp = \frac{Tv\alpha}{c_p}\triangle p,$$

since the quantities T, v, α and c_p vary very little during the process and may therefore be assumed to have constant average values independent of the pressure. Joule's results with water are very interesting and are quoted below.

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[1] We may directly deduce this result from equation (12).

Table 2.—Increase in temperature of water by increase of pressure.

Δp in kg. per cm^2	Initial temp. °C	ΔT (obs.)	ΔT (calc.)
26·19	1·20	−0·0083	−0·0071
26·19	5·00	0·0044	0·0027
26·19	11·69	0·0205	0·0197
26·19	18·38	0·0314	0·0340
26·19	30·00	0·0544	0·0563
26·17	31·17	0·0394	0·0353
26·17	40·40	0·0450	0·0476

The agreement between the observed and the calculated values is seen to be very close. This proves the essential correctness of the theory; in fact these results formed the earliest experimental verifications of the second law. The thermodynamic theory thus explains the remarkable fact that water below 4°C. cools by adiabatic compression in spite of the fact that the internal energy is thereby increased.

Another series of experiments consist in the *adiabatic stretching of wires*. The best results were obtained by Haga.[1] The change in temperature of the stretched wire was measured by means of a thermopile formed by the wire itself and another thin wire wound round it. It is well-known that tension means a negative pressure, and hence wires of substances which expand on heating, should show a cooling when stretched adiabatically. In this case the work done is not pdv but $-Fdl$, hence $\partial v/\partial T$ must be replaced by $-\partial l/\partial T$ where l is the length of the wire. Hence in place of (9) we get

$$\Delta T = -\frac{T}{C}\left(\frac{\partial l}{\partial T}\right)_F \Delta F = -\frac{T\beta}{w c_F}\Delta F, \qquad (10)$$

where β is the coefficient of linear expansion, w the mass per unit length of the wire, c_p its specific heat in mechanical units and C the heat capacity of the wire. In the above equation c_F may be replaced by c_p without serious error.

For a German silver wire of diameter 0·105 cm. at room temperature, Haga found the mean value $\Delta T = -0{\cdot}1063°$ for a tension of 13·05 kg. and $\Delta T = -0{\cdot}1725°$ for 21·3 kg. tension, giving a mean value of 0·00813 per kg. If we substitute the values of w, c_p, β in equation (10) and use the value $J = 4{\cdot}18 \times 10^7$ ergs per calorie, we get $\Delta T = -0{\cdot}00810$ in close agreement with the experimental value.

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[1] *Wied. Ann.*, Vol. 15 (1882).

India-rubber when moderately stretched has a negative expansion co-efficient. This should show a heating effect when further stretched adiabatically, which is found to be true experimentally, and may be felt even by the lips.

Exercise.—Find the change of temperature when a bar of steel 0·4 sq. cm. in section and kept at 27°C is suddenly stretched by applying a load of 200 kg. You are given the following data for steel :— co-efficient of linear expansion = 1×10^{-5} per °C., specific heat = 0·10 and density = 7·8 gm. per c.c.

7·4. Other Relations.—Besides the above two, there are other less important relations. Thus putting $x = s$, $y = v$ in (3) we get

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v . \qquad (11)$$

Again putting $x = s$, $y = p$ we get

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p \qquad (12)$$

The interpretation of these results is left to the reader.

The above relations are known as *Maxwell's four thermodynamic relations.* Besides these, there are two more relations of mathematical interest only which may be obtained by taking p, v or T, s as the pair of independent variables. They are

$$\left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial s}{\partial v}\right)_p - \left(\frac{\partial T}{\partial v}\right)_p \left(\frac{\partial s}{\partial p}\right)_v = 1. \qquad (13)$$

and

$$\left(\frac{\partial p}{\partial T}\right)_s \left(\frac{\partial v}{\partial s}\right)_T - \left(\frac{\partial p}{\partial s}\right)_T \left(\frac{\partial v}{\partial T}\right)_s = 1. \qquad (14)$$

7·5. Variation of Intrinsic Energy with Volume.—From the relation $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$, we find by substituting $\frac{du+pdv}{T}$ for ds that

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p. \qquad (15)$$

This may be called the thermodynamic equation of state of a substance and is theoretically exact. Further, this equation enables us to calculate the variation of intrinsic energy with volume.

For perfect gases, $p = RT/V$, hence $(\partial U/\partial V)_T = 0$ (Joule's law, p. 81). We see therefore that Joule's law must hold for a gas obeying the perfect gas equation.

For gases obeying van der Waals' equation $p = \frac{RT}{(V-b)} - \frac{a}{V^2}$ it can be easily seen by substituting in (15) that

$$\frac{\partial U}{\partial V} = \frac{a}{V^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Equation (16) may be used to obtain an expression for the internal energy of a van der Waals' gas. We have

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_v dT + \frac{a}{V^2} dV,$$

or

$$U = \int_0^T C_v \, dT - \frac{a}{V} + U_0, \quad . \quad . \quad . \quad (17)$$

the term $-a/V$ representing the inner potential energy of the forces of interaction between the molecules.

For general systems, we can transform (15) to a form which allows us to calculate $\partial u/\partial v$ from experimental results. This follows from equation (4) of p. 286 where it is shown that

$$\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p.$$

Hence

$$\left(\frac{\partial u}{\partial v}\right)_T = -T\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p - p$$

$$= TE\alpha - p, \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where E = bulk modulus of elasticity, α = coefficient of volume expansion.

We shall compare the ratio $\frac{\partial u}{\partial v} : p$ for a typical liquid, *viz.*, mercury. For mercury at 0°C. and atmospheric pressure we have as on p. 287, $(\partial p/\partial T)_v = 46{\cdot}5$ atmos. Hence

$$\frac{1}{p}\left(\frac{\partial u}{\partial v}\right)_T = 46{\cdot}5 \times 273{\cdot}2 - 1 = 12700.$$

Now $\partial u/\partial v$ is sometimes known as the internal pressure, and is due to the intermolecular attractions. The fact that gases condense to form liquids and solids shows that there must exist intermolecular attractions tending to pull the gas together just as the external pressure pushes it. We see here that this internal pressure is enormous in the case of solids and liquids so that it can hold the substance together even without the assistance of external pressure but when we increase the temperature, this pressure diminishes till it vanishes when the perfect gas stage is reached.

7·6. The difference $c_p - c_v$. We have

$$c_p = T\left(\frac{ds}{dT}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_v + T\left(\frac{\partial s}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p$$

Now
$$T\left(\frac{\partial s}{\partial T}\right)_v = c_v,\quad \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

$$\therefore c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p . \qquad (19)$$

This[1] is an important deduction from the second law and may be used to test it. For perfect gases[2] this yields the well-known result $c_p - c_v = R/M$. In general, however, substituting for $(\partial p/\partial T)_v$ in (19) we get

$$c_p - c_v = -T\left(\frac{\partial p}{\partial v}\right)_T \times \left(\frac{\partial v}{\partial T}\right)_p^2 = TE\alpha^2 v, \qquad (20)$$

where E is the bulk modulus of elasticity, α the coefficient of volume expansion and v the specific volume.

Equation (20) may be put in another form also. In the case of a homogeneous solid $\alpha = 3\lambda$, where λ denotes the coefficient of linear expansion. Hence (20) becomes

$$c_p - c_v = 9\lambda^2 T\, Ev . \qquad (21)$$

For solids and liquids, it is not possible to obtain c_v directly, but we can calculate it from the value of c_p with the aid of the above relationship. We give the calculations for mercury at 0°C (see p. 287). We have

$$c_p - c_v = \frac{273{\cdot}2 \times 1{\cdot}01 \times 10^6 \times (1{\cdot}81 \times 10^{-4})^2}{3{\cdot}9 \times 10^{-6} \times 13{\cdot}6 \times 4{\cdot}18 \times 10^7} = {\cdot}0041 \text{ calories.}$$

Now c_p at 0°C $= {\cdot}0333$, hence $c_v = {\cdot}0292$ and $Mc_v = 5{\cdot}84$ cal.

According to Dulong and Petit's law Mc is a constant (*vide Table* 2, page 77), but the values of c given there refer to c_p while according to the kinetic theory of matter (p. 153), $Mc_v = 3R = 5{\cdot}96$.

In most cases, the values of E and α are not available throughout the whole range of temperature, and extrapolated values are used for the verification of (20). But for at least one case, *viz.*, liquid hydrogen all the quantities are available due to the researches of Eucken (*V. D. Phys. Gesell.* **18**, 1, 1916). For this substance we have at 20·4°K.

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[1] We can get this relation also by combining equation (14) of Chap. V and equation (15) of this chapter.

[2] For a real gas we must employ the actual equation of state (Chap. X).

the following data :—$C_p = 4 \cdot 53$ cal./deg. mol., $C_v = 2 \cdot 83$ cal./deg. mol. The volume of a gram-molecule $= 28 \cdot 2$ c.c., $\alpha = 1 \cdot 60 \times 10^{-2}$ per °C., $E = 5 \cdot 13 \times 10^{2}$ kg/cm.^{2} Hence we have

$$\frac{T\alpha^2 V}{J} E = \frac{20 \cdot 4 \times 28 \cdot 2 \times (1 \cdot 60 \times 10^{-2})^2 \times 5 \cdot 13 \times 10^3 \times 10^3 \times 981}{J}$$

$$= 1 \cdot 77 \text{ cal./deg.}$$

The experimentally obtained difference is 1·70 cal./deg. Hence equation (20) is verified.

Nernst and Lindemann[1] applied formula (20) to calculate c_v for ordinary metals, and found that for the ordinary range of temperatures Mc_v was nearly equal to 3R. In certain cases however there is a large departure from the law. In order to explain these a more satisfactory theory has been developed (see Chap. XVI).

A few values of C_v calculated according to formula (20) are given in the following Table.[2]

Table 3.—Calculated values of C_v for solids.

Metal	Volume of gram-atom in c.c.	$\alpha \times 10^6$ per °C	$\frac{1}{E} \times 10^{-12}$ in cm.^{2} dyne.$^{-1}$	C_p in cal. °C^{-1} mol^{-1}	$\frac{C_p}{C_v} = \gamma$	C_v in cal. °C^{-1} mol^{-1}
Al	10·0	72	1·48	5·84	1·042	5·61
Cu	7·1	48	0·785	5·79	1·025	5·65
Ag	10·3	55	0·775	5·93	1·047	5·67
Pb	18·3	82	2·4	6·39	1·055	6·06
Pt	9·1	27	0·40	6·24	1·019	6·13

According to Grüneisen (Chap. XIII), α is proportional to c_p and if we take $Ev =$ constant for any one metal, we can deduce the empirical law

$$c_p - c_v = Ac_p^2 T,$$

where A is a constant characteristic of the element. This relation may be used to calculate c_v at any temperature.

7·7. Variation of c_v with Volume :—From the relation

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

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[1] *Zeits. f. Electrochem.*, **17**, 819, 1911.

[2] The table is taken from Jellinek, *Lehrbuch der physikalischen Chemie*, Vol. 2, p. 246.

we obtain by partial differentiation with respect to T

$$\frac{\partial^2 s}{\partial T \partial v} = \left(\frac{\partial^2 p}{\partial T^2}\right)_v.$$

Now $$c_v = T\left(\frac{\partial s}{\partial T}\right)_v.$$

$$\therefore \quad \left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v. \quad . \quad . \quad . \quad (22)$$

This equation can be verified if we know an accurate equation of state. Kuenen found experimentally that c_v increases with v to a maximum and then decreases. Assuming the gas to obey van der Waals' equation we have $\left(\frac{\partial^2 p}{\partial T^2}\right) = 0$, whence $\left(\frac{\partial c_v}{\partial v}\right)_T = 0$, or c_v = constant at the same temperature for all volumes. Dieterici's equation does give a variation of c_v but no maximum as observed by Kuenen.

7·8. Variation of c_p with Pressure.—From the relation

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p,$$

we obtain by partial differentiation with respect to T and certain other steps,

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p. \quad . \quad . \quad . \quad . \quad (23)$$

A good numerical illustration of (23) is given by the observed variation of C_p for superheated water vapour (see Landolt-Börnstein, *Tabellen*, pp. 1276 and 1324, 5th Ed). It was found by Knoblauch and Raisch that at 155°C. the gram-molecular specific heat in calories is given by $C_p = 8 \cdot 48 + 0 \cdot 252\ p$, where p is expressed in kg/cm².

$$\therefore \left(\frac{\partial C_p}{\partial p}\right)_T = \frac{0 \cdot 252 \times 4 \cdot 18 \times 10^7}{981 \times 10^3} \; \frac{\text{ergs}}{\text{dyne/cm}^2} = 10 \cdot 4 \text{ c.c./deg.}$$

Again it was found by Jacob that between 110° and 200°C. we have for a gram-molecule under a pressure of 1 kg/cm².

$$\left(\frac{\partial V}{\partial T}\right)_p = 90 \cdot 5 - 0 \cdot 023\ \theta.$$

where θ is the temperature in °C. and the volume is expressed in c.c.

$$\therefore -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p = 428 \times 0 \cdot 023 = 9 \cdot 85 \text{ c.c./deg.}$$

Hence the values of $\left(\frac{\partial C_p}{\partial p}\right)_T$ and $-T\left(\frac{\partial^2 V}{\partial T^2}\right)_p$ are seen to agree very closely.

From (23) and (22) it follows that

$$C_p = (C_p)_0 - \int_0^p T\left(\frac{\partial^2 V}{\partial T^2}\right)_p dp. \quad . \quad . \quad . \quad (24)$$

and

$$C_v = (C_v)_\infty + \int_\infty^v T\left(\frac{\partial^2 p}{\partial T^2}\right)_v dv, \quad . \quad . \quad . \quad (25)$$

where $(C_p)_0$ and $(C_v)_\infty$ denote the specific heats extrapolated to the zero pressure, *i.e.*, to the state of a perfect gas. These formulæ are used to calculate the specific heat of a perfect gas, *i.e.*, for pressure tending to zero, from the observed values of specific heat of real gases at some finite pressure. Various semi-empirical methods are used to represent the variation of c_p with pressure, and c_v with volume. For further details see Eucken, *Chemische Physik*, p. 173.

PROBLEMS[1]

1. Prove that for any substance the ratio of the adiabatic and isothermal elasticities is equal to the ratio of the two specific heats.

We have from definition

$$E_T = -v\left(\frac{\partial p}{\partial v}\right)_T; \quad E_s = -v\left(\frac{\partial p}{\partial v}\right)_s.$$

$$\therefore \frac{E_s}{E_T} = \frac{\left(\frac{\partial p}{\partial v}\right)_s}{\left(\frac{\partial p}{\partial v}\right)_T} = \frac{\left(\frac{\partial p}{\partial T}\right)_s \left(\frac{\partial T}{\partial v}\right)_s}{\left(\frac{\partial p}{\partial s}\right)_T \left(\frac{\partial s}{\partial v}\right)_T}$$

$$= \frac{\left(\frac{\partial T}{\partial v}\right)_s \left(\frac{\partial s}{\partial p}\right)_T}{\left(\frac{\partial T}{\partial p}\right)_s \left(\frac{\partial s}{\partial v}\right)_T} = \frac{\left(\frac{\partial p}{\partial s}\right)_v \left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial v}{\partial s}\right)_p \left(\frac{\partial p}{\partial T}\right)_v}$$

from the four thermodynamic relations.

$$\therefore \frac{E_s}{E_T} = \frac{(\partial s/\partial T)_p}{(\partial s/\partial T)_v} = \frac{(\partial Q/\partial T)_p}{(\partial Q/\partial T)_v} = \frac{c_p}{c_v} = \gamma.$$

2. Prove that the ratio of the adiabatic to the isobaric coefficient of expansion is $1/(1-\gamma)$.

We have $\frac{(\partial v/\partial T)_s}{(\partial v/\partial T)_p} = \frac{1}{\left(\frac{\partial T}{\partial v}\right)_s \left(\frac{\partial v}{\partial T}\right)_p} = \frac{1}{-\left(\frac{\partial p}{\partial s}\right)_v \left(\frac{\partial v}{\partial T}\right)_p}$

$$= \frac{1}{-\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial s}\right)_v} = \frac{T\left(\frac{\partial s}{\partial T}\right)_v}{-(c_p - c_v)} \text{ from (19)} = \frac{1}{1-\gamma}.$$

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[1] For a list of the important thermodynamic relations see Bridgman, "*A Condensed Collection of Thermodynamic Formulas*," Harvard University Press, or Bridgman, *Phys. Rev.*, Vol. 3, p. 273 (1914).

3. Prove that the ratio of the adiabatic to the isochoric pressure coefficient of expansion is $\gamma/(\gamma-1)$.

We have $\dfrac{(\partial p/\partial T)_s}{(\partial p/\partial T)_v} = \dfrac{1}{\left(\dfrac{\partial T}{\partial p}\right)_s\left(\dfrac{\partial p}{\partial T}\right)_v} = \dfrac{1}{\left(\dfrac{\partial v}{\partial s}\right)_p\left(\dfrac{\partial p}{\partial T}\right)_v}$

$$= \frac{1}{\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial T}{\partial s}\right)_p} = \frac{T\left(\frac{\partial s}{\partial T}\right)_p}{(c_p-c_v)} = \frac{\gamma}{\gamma-1}.$$

4. Deduce equations giving the relation between p, v; v, T, and p, T for adiabatic changes in an imperfect gas.

Use the results of Ex. 1 to 3, and substitute the values of the differentials $(\partial p/\partial V)_T$, $(\partial V/\partial T)_p$ and $(\partial p/\partial T)_v$ occurring therein by using the equation of state of a gas. Using the equation in the form $pV = RT + Bp$ it can be shown that

$$\frac{dp}{p} = -\gamma\frac{dV}{V-B},$$

$$(\gamma-1)\frac{dV}{V-B} = -\frac{dT}{T}\left(1 + \frac{T}{V-B}\frac{dB}{dT}\right),$$

$$\frac{\gamma-1}{\gamma}\cdot\frac{dp}{p} = \frac{dT}{T}\left(1 + \frac{p}{R}\frac{dB}{dT}\right),$$

which give the relations for infinitesimal adiabatic changes. Assuming γ to be constant, the first of these can be integrated, yielding $p(V-B)^{\gamma} =$const. while the other two cannot be integrated. The last equation is important as it has to be utilised in the experiments of Lummer and Pringsheim, Partington and others (p. 95).

5. Writing the equation for δQ in the form

$$\delta Q = \left(\frac{\partial u}{\partial T}\right)_v dT + \left\{\left(\frac{\partial u}{\partial v}\right)_T + p\right\} dv = c_v\,dT + l\,dv$$

where l is the latent heat of isothermal expansion per unit increase of volume, prove that

$$l = \frac{L}{(v_2-v_1)} = T\left(\frac{\partial p}{\partial T}\right)_v$$

and
$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v.$$

$$\left[\text{Now } ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv = \frac{c_v}{T}dT + \left(\frac{\partial p}{\partial T}\right)_v dv.\right.$$

This is often called the first Tds equation.

Comparing this with the expression for δQ given above (since $\delta Q = Tds$) we have

$$l = T\left(\frac{\partial p}{\partial T}\right)_v .$$

Again $ds = \frac{1}{T}(c_v dT + l dv)$. Now since ds is a perfect differential we have

$$\frac{\partial}{\partial v}\left(\frac{c_v}{T}\right) = \frac{\partial}{\partial T}\left(\frac{l}{T}\right) = \left(\frac{\partial^2 p}{\partial T^2}\right)_v \Big].$$

6. (a) Use the result obtained in the previous question to show that the entropy of the van der Waals' gas is

$$s = \int \frac{c_v dT}{T} + R\, ln\,(v-b) + s_0.$$

(b) Prove that the temperature change during free expansion of a van der Waals' gas is $\triangle T = \frac{a}{c_v}\,\frac{v_i - v_f}{v_i\, v_f}$.

7. Prove the second $T\,ds$ equation

$$T\,ds = c_p\,dT - T\left(\frac{\partial u}{\partial T}\right)_p dp.$$

Hence deduce equation (23).

[$T\,ds = T\left(\frac{\partial s}{\partial T}\right)_p dT + T\left(\frac{\partial s}{\partial p}\right)_T dp = c_p\,dT - T\left(\frac{\partial v}{\partial T}\right)_p dp$ and ds is a perfect differential.]

8. Using the result of the last exercise calculate (a) the heat given out when the pressure on 200 gm. of copper is increased reversibly and isothermally from zero to 1000 atmos. at 27°C, (b) the work done during the above compression, (c) the rise in temperature if the above compression had been performed in a reversible adiabatic manner. You are given the following data for copper :—Density= 8·9 gm/cc. ; coefficient of volume expansion $= 49 \times 10^{-6}$ per °C; Isothermal compressibility $= 0{\cdot}776 \times 10^{-12}$ cm.^{2}/dyne and $c_p = 0{\cdot}093$ cal. gm.$^{-1}$ °C^{-1}.

9. Prove that

$$(c_p - c_v)\frac{\partial^2 T}{\partial p \partial v} + \frac{\partial c_p}{\partial p}\,\frac{\partial T}{\partial v} - \frac{\partial c_v}{\partial v}\,\frac{\partial T}{\partial p} = 1.$$

10. Deduce from the relation

$$\frac{\partial c_u}{\partial v} = T\,\frac{\partial^2 p}{\partial T^2}$$

the relation

$$c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p.$$

11. Using the two expressions for ds given in problems 5 and 7, deduce equation (19).

12. Prove that

$$\left(\frac{\partial u}{\partial v}\right)_p = c_p\left(\frac{\partial T}{\partial v}\right)_p - p.$$

13. Prove that for a gas obeying the relation

$$pV = RT + Bp,$$

$$C_p - C_v = R + 2p\frac{dB}{dT}.$$

14. The pressure on 10 gm. of water at 0°C is increased reversibly and adiabatically from 0 to 1000 atmos. Calculate the change in temperature, given that the coefficient of volume expansion $= -67\times10^{-6}$ $°C^{-1}$, $c_p = 1\cdot0087$ cal. $gm.^{-1}\,°C^{-1}$; specific volume $= 1\cdot000$ $cm.^3/gm.$

[Use eqn. (9)].

15. If in the last example the compression is brought about reversibly and isothermally, calculate (a) the heat transferred and (b) the work done. (Isothermal compressibility $= 43\times10^{-12}$ $cm.^2/dyne$).

[For part (a) use equation (8); and for part (b) proceed thus :—

$$\text{Work} = \int p\,dv = \int p\left(\frac{\partial v}{\partial p}\right)_T dp = -\frac{v\kappa}{2}(p_f^2 - p_i^2)$$ where κ is the isothermal compressibility].

16. Prove that for a thin liquid film

$$2\left(\frac{\partial \mathscr{T}}{\partial p}\right)_{A,T} = \left(\frac{\partial v}{\partial A}\right)_{p,T}$$

where $\mathscr{T}$ denotes the surface tension and A the area of the film.

[Start from the relation $\delta Q = du + p\,dv - 2\mathscr{T}dA = T\,ds$ and take p and A as the independent variables and assume T to be constant.]

17. Apply the two laws of thermodynamics to a thermo-electric circuit made up of two metals a, b and having the temperatures of the two junctions as T, $T+dT$ and show that

$$\pi = T\frac{\partial E}{\partial T} \text{ and } \sigma_a - \sigma_b = -T\frac{\partial^2 E}{\partial T^2}.$$

where dE is the electromotive force developed, and π, σ the Peltier and the Thomson coefficients respectively.

[Assume a small current i to flow in the circuit from a to b through the hot junction at $T+dT$. Then due to Peltier electromotive force the heat absorbed at the hot junction is $i(\pi+d\pi)$ per second, that given out at the cold junction is πi. Due to Thomson electromotive force the heat absorbed in a is $i\sigma_a dT$, that given out in b is $i\sigma_b dT$ per second. The work done by the couple is $i\,dE$ per second where dE is the E. M. F. generated in the circuit. This work must be supplied from the thermal energy gained by the circuit. Hence from the first law

$$dE = d\pi + (\sigma_a - \sigma_b)dT.$$

Again from the second law

$$\frac{\pi + d\pi}{T + dT} - \frac{\pi}{T} + \frac{(\sigma_a - \sigma_b)dT}{T} = 0.$$

Combining these we get the required results.]

18. The tension in a copper wire of mass 5 gm., diameter 1 mm. and temperature 0°C is increased reversibly and isothermally from zero to 10^8 dynes. Calculate the heat transferred. What would be the temperature change if the process were performed reversibly and adiabatically? You are given the following data :—

Density = 8·93 gm./c.c., coefficient of linear expansion = $16 \cdot 8 \times 10^{-6}$ $°C^{-1}$, $c_p = 0 \cdot 091$ cal. gm^{-1}. $°C^{-1}$.

19. A double film of water of mass 4 gm. and at a temperature of 27°C is stretched reversibly and adiabatically from an area of 10 sq. cm. to 50 sq. cm. Calculate the resulting change in temperature, given that temperature coefficient of surface tension = $-$ 0·245 dynes cm^{-1}. $°C^{-1}$, $c_A = 1$ cal. gm^{-1} $°C^{-1}$.

BOOKS RECOMMENDED

Same as in Chapter V.

CHAPTER VIII

THERMODYNAMICAL EQUILIBRIA OF PHYSICAL AND CHEMICAL SYSTEMS

THERMODYNAMICAL FUNCTIONS

8·1. Tendency of Thermodynamical Systems towards Equilibrium.—In §5·3 we have already defined a thermodynamical system as one whose interaction with the surroundings can only be partly thermal and partly mechanical *i.e.*, all such interactions consist in a flow of heat from one to the other and the performance of work by one on the other. Such a system may or may not be in thermodynamical equilibrium. A thermodynamical system may, in addition to its interaction with the surroundings, itself undergo physical or chemical changes (Reactions) as a result of the mutual interaction amongst the particles constituting the system. Such, for example, is a solid or liquid giving off its vapour, or a number of chemical substances like NH_3 and HCl, reacting with each other and producing new substances, NH_4Cl in this case, or electromotive forces being generated in a cell like the Daniell cell, as a result of the chemical reactions taking place in the cell. The question now is whether from a knowledge of the macroscopic properties alone we can determine the spontaneous changes taking place in the system and their direction.

Experience tells us that in such cases, though interaction between the constituent molecules or atoms are incessantly taking place, yet after sufficiently long time, a condition of macroscopic equilibrium sets in which is a function of the coordinates defining the thermodynamical state of the system, *viz.*, its temperature, pressure, concentration of the reacting substances. In other words all thermodynamical systems have an inherent tendency to change in such a direction as to attain the equilibrium state. Consider, for example, water in a vessel connected to a pump. When we evacuate the vessel, and shut off the pump, water begins to evaporate till a certain pressure is reached in the vessel. This is the "equilibrium pressure" for that temperature. If some vapour be pumped out, more water will evaporate till the saturation pressure is reached; if the vapour be compressed, some of it will be condensed till the gas pressure reduces to the saturation pressure. It will now be shown how the equilibrium condition—in this case the saturation pressure at the required temperature—can be determined from general thermodynamical considerations. The guiding principles in such cases are the two laws of thermodynamics.

The two laws, as already enunciated in Chaps. V and VI, do not directly enable us to determine the direction of spontaneous changes. The first law simply tells us that one type of energy may be converted into another type and the transformation may proceed as well in one direction as in the other. The second law goes a little further and states that only such transformations can take place for which the entropy does not decrease. It, therefore, excludes a large number of possible changes, but still it does not say whether those changes in which entropy would increase do necessarily occur. The various formulations of the second law given in Chap. VI merely state that such changes are permissible; they, however, leave the question open whether these permissible changes do actually occur. In fact those formulations of the second law did not state the fundamental fact of experience that all thermodynamical systems have an inherent tendency towards the equilibrium state. The two laws as formulated above therefore require to be supplemented by two simple rules obtained as a result of experience which take into account this inherent tendency of systems. These rules are the following :—In the first place the internal energy *U* is of the nature of potential energy (occurring in dynamics) and therefore in analogy with dynamical principles, an isolated thermodynamical system will so alter itself, if permitted by the constraints, that its internal energy tends to decrease, a part of this energy being converted into energy of non-potential nature. In other words *U* tends towards a minimum. In the second place the entropy of an isolated system increases spontaneously, equilibrium being reached when the entropy has attained its maximum value. This second rule may be regarded as forming part of the second law itself and asserts the inherent tendency of isolated systems to change towards equilibrium state and fixes the direction of this spontaneous change.

8·2. Conditions of Natural Change.—Let us suppose that the system A is placed in contact with the surrounding medium B (air, containing vessel, etc., ...). As was proved in § 6·12, for all possible changes occurring in the whole system consisting of the surrounding medium as well as A, we have

$$\delta S + \delta S_0 \geqq 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where δS, δS_0 denote the increase in entropy of A and B respectively. This condition determines the direction of the change. The sign of equality refers to the ideal limiting case, when the changes are brought about by a reversible process.

If we further assume that all changes in the surrounding medium are reversible[1], we have for any change

$$\delta S_0 = -\frac{\delta Q}{T},$$

where δQ is the heat absorbed by A from B.

Now from the first law

$$\delta Q = \delta U + \delta W,$$

where δU denotes the increase in internal energy of A and δW the work done by it. Hence equation (1) yields

$$\delta S - \frac{\delta U + \delta W}{T} \geqq 0, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

---

[1] Since the surrounding medium is very large it does not change appreciably in temperature due to small changes occurring in the system. Hence the transfer of heat will be reversible. This is particularly so in the case of isothermal changes with which we shall mostly deal in this chapter because then the system and the surroundings (*e.g.*, bath) are maintained always at the same temperature. We may suppose the transfer of heat to be brought about by reversible changes of volume of the surrounding medium. These postulates are not far from what actually holds in practice. Hence, the assumption of reversibility in the general case is justified. If the changes are not exactly reversible, δS_0 is greater than $-\delta Q/T$ by a small amount ϵ whose magnitude depends upon the degree of irreversibility introduced and may be neglected in general. It will be seen that the condition (2) with the sign of inequality for a naturally occurring process is more comprehensive and includes the case of a finite ϵ for if $\delta S - (\delta U + \delta W)/T > 0$, then certainly $\delta S - (\delta U + \delta W)/T + \epsilon > 0$ is satisfied and the change takes place.

or, for an infinitesimal change,

$$dU - TdS \leqq -dW. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This is the most general condition for natural changes occurring in a system of bodies. We have already stated at the end of §8·1 that such changes are not only permissible but do actually take place when permitted by the external constraints on the system. We shall now select a few particular case of (3).

8·3. Adiabatic Processes.—Here $\delta Q = 0$ and hence (3) reduces to

$$dS \geqq 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

i.e., the entropy of an isolated system (isolated thermally as well as dynamically) remains constant in reversible processes and increases in irreversible processes. Such a system has no interactions either thermal or mechanical with the surroundings and for it both U and V remain constant. This has already been discussed.

8·4. Isothermal Processes.—Let us now consider processes in which the system exchanges heat with the surroundings (as in a heat bath) and is thereby maintained at a constant temperature T. In this case, (3) can be written in the form

$$d(U - TS) \leqq -dW.$$

Let us define a function $F = U - TS$. Then

$$dF \leqq -dW. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

F has been called *Free Energy* by Helmholtz and *Thermodynamic Potential*[1] at constant volume by W. Gibbs. Unfortunately the use of the term free energy for this function has produced considerable confusion in the literature and is somewhat misleading as it is not always equal to the part of the internal energy freed during reversible processes for mechanical work as assumed by Helmholtz. It may be more appropriately called Available Energy or Work Function since equation (5) shows that for reversible changes the work done by the system is equal to the decrease in this F function. For irreversible changes the work done by the system is less than the decrease in F. We shall call F as Helmholtz's free energy or available energy.

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[1] The reason why it is called potential is that it is analogous to the term potential employed in dynamics in the sense that the difference in potential of two states gives the work done in passing from one state to the other by a reversible process (from eqn. 5).

8·5. Isothermal-Isochoric Reactions.—If in addition the system is dynamically insulated (but not thermally) by enclosing it in a container with invariable volume, the external work done is zero, and hence

$$dF \leqq 0. \qquad \ldots \ldots \qquad (6)$$

The upper sign denotes an irreversible change which is more usual and natural, while the lower sign denotes a reversible change. Thus in a natural isothermal change at constant volume Helmholtz's free energy decreases.

For a majority of chemical reactions the change in U is much greater than the change in TS, and hence (6) reduces to

$$dU \leqq 0, \qquad \ldots \ldots \qquad (7)$$

i.e., heat is evolved in actual reactions. This yields the principle of Berthelot which may be stated :—*Chemical reactions in which the external work is zero take place in such a manner that heat is always evolved in reactions.* The principle cannot be universal for that would make endothermic reactions (reactions in which heat is absorbed, *e.g.*, in the formation of HI out of H_2 and I_2) impossible. This point is further dealt with in Chap. XVIII.

From the definition of F, *viz.*,

$$F = U - TS,$$

we have

$$dF = dU - TdS - SdT = -pdV - SdT.$$

$$\therefore \left(\frac{\partial F}{\partial V}\right)_T = -p; \left(\frac{\partial F}{\partial T}\right)_V = -S. \qquad \ldots \qquad (8)$$

Hence

$$F = U + T\left(\frac{\partial F}{\partial T}\right)_V \qquad \ldots \ldots \qquad (9)$$

It will be seen from equation (8) that the thermodynamical properties of the system are uniquely determined by the function F which may be used directly in place of S for studying the thermodynamics of the change. This was pointed out by

Massieu, who called the equation $F = f(V, T)$ the 'fundamental equation' for the substance.

If the isothermal change be finite, say from state 1 to state 2, then we shall have from (9)

$$F_2 - F_1 = U_2 - U_1 + T\frac{\partial}{\partial T}(F_2 - F_1),$$

or

$$\Delta F = \Delta U + T\left[\frac{\partial}{\partial T}\Delta F\right]_V \quad . \quad . \quad . \quad . \quad . \quad (10)$$

But from (5) $-\Delta F = A$ where A is the maximum work obtainable from the system, *i.e.*, that during a reversible change. Also $-\Delta U = U_r$ from the first law where U_r is the heat of reaction at constant volume. Hence (10) yields

$$A - U_r = T\frac{dA}{dT} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Equations (9) and (11) are called Gibbs-Helmholtz equation and are of great importance experimentally in calculating the variation of A with temperature.

8·6. Application to Thermochemistry. E.M.F. of Reversible Galvanic Cells.—The Free Energy theorem expressed by equation (6), is best illustrated in its application to Thermochemistry, *e.g.*, in the calculation of the E.M.F. of galvanic cells from the chemical reaction involved.

Daniell Cell.—For illustration, we consider the Daniell cell which is shown schematically in Fig. 1. It consists of a glass vessel with a copper plate in the centre which dips in copper sulphate solution. On the outer side is a Zn-plate dipping in zinc sulphate solution. The two are separated by a porous clay vessel, the function of which is to prevent quick mixing of the two salts.

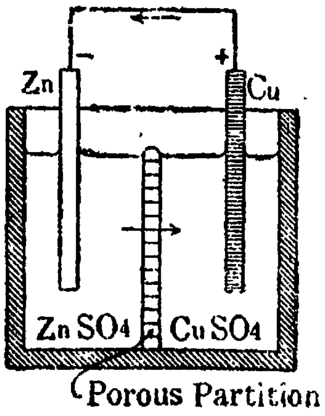

Fig. 1.—Schematic diagram of the Daniell cell.

When the two plates are connected by a wire a current passes from Cu to Zn through the wire outside the cell, and from Zn to Cu inside the cell. The E.M.F. is found to be 1·09 volts. The passage of the current is attended with chemical reactions. Zinc goes into solution and copper is deposited on the Cu-plate. With the passage of

96450 coulombs, ½ gram-atoms (32·5 gm.) of Zn pass into solution, and ½ gram-atoms (31·5 grams) of Cu get deposited.

The reaction is of the type

$$\mathrm{Cu} \mid \mathrm{CuSO_4}\ \text{sol.} \mid \mathrm{ZnSO_4}\ \text{sol.} \mid \mathrm{Zn}.$$

The total chemical reaction is

$$[\mathrm{Zn}] + \mathrm{CuSO_4}\ (\text{aq.}) = [\mathrm{Cu}] + \mathrm{ZnSO_4}\ (\text{aq}).$$

In this process chemical energy is being converted to electrical energy. The chemical energy evolved in the process can be worked out from the following two equations:—

$$[\mathrm{Zn}] + \mathrm{H_2SO_4}(\text{aq.}) = \mathrm{ZnSO_4}(\text{aq.}) + \mathrm{H_2} + 248{,}500\ \text{cal.}$$

$$[\mathrm{Cu}] + \mathrm{H_2SO_4}(\text{aq.}) = \mathrm{CuSO_4}(\text{aq.}) + \mathrm{H_2} + 198{,}370\ \text{cal.}$$

Combining the above two we get

$$[\mathrm{Zn}] + \mathrm{CuSO_4}(\text{aq.}) = [\mathrm{Cu}] + \mathrm{ZnSO_4}(\text{aq.}) + 50{,}130\ \text{cal.}$$

It was first suggested by W. Thomson (Lord Kelvin) that the E.M.F. of the cell may be calculated from the first law if we suppose that the whole of this energy is being converted to electrical energy. Supposing this to be the case, we can easily calculate the E.M.F.

$$\begin{aligned} \text{The electrical energy} &= \text{E.M.F.} \times \text{quantity of electricity passed} \\ &= E \times 96{,}450 \times 2 \times 10^7\ \text{ergs,} \end{aligned}$$

where E is the E.M.F. developed in volts, 96,450 the charge in coulombs carried by the equivalent weight and 2 is the valency of the ion. This must equal the energy of chemical reaction, *i.e.*, $= 50{\cdot}13 \times 10^3 \times 4{\cdot}186 \times 10^7$ ergs. Hence

$$E = 1{\cdot}09\ \text{volts.}^1$$

But Gibbs and Helmholtz showed that since the process is isothermal-isochoric as described in §8·5, the external work obtained should be equivalent to the change in *free energy,* not the change in *total energy,* provided of course the cell can be regarded as reversible; or in symbols $EB \neq (-\Delta U)$ as was wrongly assumed by Thomson but

$$EB = -\Delta F = A, \quad . \quad . \quad . \quad . \quad (12)$$

where B is the quantity of electricity that passes through the circuit.

Substituting this value of A from (12) in (11) we get

$$E - T\left(\frac{\partial E}{\partial T}\right)_v = \frac{U_r}{B}, \quad . \quad . \quad . \quad . \quad (13)$$

---

[1] From these relations it will be easily seen that for a monovalent ion (valency 1) an E.M.F. of 1 volt corresponds to 23,050 calories of energy.

where E and B should be expressed in electromagnetic units and U_r in ergs. If E is expressed in volts and U_r in calories, and n denote the valency of the element, this yields

$$E-T\left(\frac{\partial E}{\partial T}\right)_v=\frac{U_r\times 4\cdot 186\times 10^7}{96450\times n\times 10^7}=\frac{U_r}{23050\,n}, \qquad (14)$$

since $B=n\times 96450$ coulombs. This is the general equation of E. M. F. of reversible galvanic cells.

We shall apply eqn. (14) to the Daniell cell. From very accurate and careful investigations Jahn found that $U_r=25055$ cal. at 0°C, while $E=25{,}263$ cal. at 0°C, calculated from the value of $E=1\cdot 096$ volts. $\partial E/\partial T$ was experimentally found to be $3\cdot 4\times 10^{-5}$ volt/deg. Hence,

$$T\,\frac{\partial E}{\partial T}=273\times 3\cdot 4\times 10^{-5}=9\cdot 28\times 10^{-3}\text{ volts.}$$

Expressed in calories, this is equal to 213 cal, while $E-U_r=208$ cal. Thus equation (14) is verified. The reason why Thomson's calculation, though wrong, gave approximately correct value in the case of Daniell cell is that in this case $\partial E/\partial T$ is very small.

Clark Cell.—In the well-known Clark cell we have the reaction :—

$$[\mathrm{Zn}]+\mathrm{Hg_2SO_4.\ 7H_2O}\ (\text{solid})=\mathrm{ZnSO_4.\ 7H_2O}\ (\text{solid})+2\mathrm{Hg}.$$

The energy-relation in this reaction has been very carefully measured by V. Steinwehr, and U_r has been found to be 81,130 cal. The E.M.F. at 18°C. is found to be 1·4288 volts, corresponding to the value of $A=65{,}880$ cal. It is therefore quite clear that $EB\neq U_r$.

According to the electrical measurements of Jaeger and Kahle

$$E_t=1\cdot 4324-1\cdot 19.\ 10^{-3}(t-15)-7\times 10^{-6}(t-15)^2\text{ volts.}$$

Hence $\qquad \partial E/\partial T=-1\cdot 23\times 10^{-3}$ at $t=18$°C.

Or $\qquad T(\partial E/\partial T)=-1\cdot 23\times 10^{-3}\times 291=-0\cdot 3579.$

From eqn. (14)

$$\frac{U_r}{2\times 23050}=E-T\,\frac{\partial E}{\partial T}=1\cdot 4288+0\cdot 3579=1\cdot 7867$$

which gives $U_r=82{,}410$ cal. This agrees very well with the experimentally observed value 81,130.[1]

In Table 1 the data for a few reversible galvanic cells are given which show clearly that the Gibbs-Helmholtz relation is fully confirmed by the results of experiments.

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[1] For full description of the energetics of the Clark cell, see Jellinek, *Lehrbuch der Physikalischen Chemie*, Vol. 3, p. 729 (1930 edition).

Table 1.—*E. M. F. and heat of reaction for some reversible cells at* 0°C.

Elements of the cell	E (in volts)	$\frac{\partial E}{\partial T}\left(\frac{\text{volt}}{\text{deg.}}\right)$	U_r in cal. from (13)	U_r in cal.(obs.)	$A=EB$ in cal.
$Ag/AgCl$ $Zn/ZnCl_2.50H_2O$	1·0171	$-2{\cdot}1\times10^{-4}$	49540	49080	46890
$Ag/AgBr$ $Zn/ZnBr_2.25H_2O$	0·84095	$-1{\cdot}06\times10^{-4}$	40100	39940	38765
Hg/Hg_2Cl_2+KCl Hg/Hg_2O+KOH	0·1483	$+8{\cdot}37\times10^{-4}$	−3700	−3280	6840

8·7. Reversible and Irreversible Cells.—The Daniell cell is of the reversible type, *i.e.*, the whole process can be reversed by reversing the direction of the current. If the outer circuit of the cell contains an external E.M.F., and if a current is sent from Cu to Zn in the solution, then Cu goes into solution, the concentration of $CuSO_4$ will be increased, and Zn will be deposited from the $ZnSO_4$ solution on the Zn plate. This is exactly the opposite of what takes place when the current is allowed to flow from Zn to Cu in the solution.

On the other hand, the original cell of Volta

$$Zn \mid H_2SO_4(aq.) \mid Cu$$

where Zn and Cu plates are dipped in H_2SO_4 solution, is irreversible. Here Cu is the positive plate, Zn is negative. If they are connected by a wire, current passes from Cu to Zn on the outside, and from Zn to Cu in the inside. Zn goes into solution, and hydrogen is evolved at the Cu-electrode. If a current be sent in the opposite direction, Cu goes into solution and H_2 is evolved on the Zn-plate. So the conditions are not reversed by reversing the current.

Another important type of reversible cell is the concentration cell in which the E. M. F. is developed not by the contact of two different substances but two solutions of the same substance having different concentrations. We cannot however enter into this subject here.

8·8. Isothermal-Isobaric Processes.—In many thermodynamical transformations the temperature and pressure of the system always remain constant being equal to the temperature and pressure of the surroundings. This is so in many chemical reactions where the temperature is maintained constant by a suitable heat-bath while the pressure is that of the earth's atmosphere. In such cases the external work done is due to changes in volume. Hence $dW = pdV$, and the condition (5) for an isothermal process becomes

$$dF \leqq -pdV,$$

$$d(U-TS+pV) \leqq 0.$$

The function $G = U+pV-TS$ is known as the thermodynamic potential at constant pressure or Gibbs' function. Hence the condition of change is

$$dG \leqq 0. \qquad (15)$$

Further from the definition of G we observe that

$$dG = Vdp-SdT.$$

$$\therefore \left(\frac{\partial G}{\partial p}\right)_T = V, \quad \left(\frac{\partial G}{\partial T}\right)_p = -S, \qquad (16)$$

and

$$G = (U+pV)+T\left(\frac{\partial G}{\partial T}\right)_p \qquad (17)$$

8·9. General Conditions of Thermodynamical Equilibrium.—The theory[1] of thermodynamical equilibrium was developed by Gibbs on lines similar to the mechanical theory of statics by Lagrange. We have already investigated in the foregoing sections the conditions which have to be satisfied in order that changes can take place in a system under given external conditions. Now if the system is in such a state that these conditions cannot be satisfied, no change will take place. That is, the system will be in equilibrium. This is the most general condition of equilibrium and may be mathematically stated :— "*If for any virtual*[2] *infinitesimal change δ of a system, the condition for natural change represented by the inequality in equation* (3) *is not satisfied, the system will be in stable equilibrium.*

Adiabatic process.—For an isolated system for which both U and V remain constant, the condition of change is expressed by

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[1] For a detailed discussion of this theory see Keenan, *Thermodynamics*, Chaps. XXIII, XXIV and XXV.

[2] 'Virtual' is here used in the same sense as in Mechanics and virtual change means all conceivable variations of the system subject of course to the external constraints but irrespective of whether they conserve the equilibrium or produce unstable states. The differential d refers to an *actual* infinitesimal change of state which must therefore connect two states of equilibrium. The change δ therefore includes the change d.

$dS > 0$ from (4). We have omitted the sign of equality as it refers to the ideal case of a reversible process which does not occur in nature. Hence the condition[1] of equilibrium of an isolated system is

$$\delta S \leqq 0. \qquad (18a)$$

In general however any infinitesimal virtual change consistent with the external conditions can be reversed if the sign of all the variations be changed. Hence if the changes $\delta S < 0$ is possible, the change $\delta S > 0$ is also possible and the system will not be in equilibrium. Thus the condition for equilibrium reduces to

$$\delta S = 0. \qquad (18b)$$

Hence in all adiabatic changes of a system, the states of stable equilibrium are given by the condition that the entropy is a maximum.[2] It cannot be a minimum, for then changes will take place quickly. Hence the further condition for stable equilibrium is $\delta^2 S < 0$. The entropy may have several maxima and hence there may be several states of stable equilibrium. That equilibrium is absolutely stable for which the entropy is an absolute maximum.

If the change is adiabatic-isochoric, we have in addition to (18b), the conditions of equilibrium $\delta V = 0$, $\delta U = 0$. If it is adiabatic-isobaric the additional conditions are $\delta p = 0$, $\delta H = 0$. These results follow readily from eqn. (3).

For *isothermal-isochoric* reactions the condition of stable equilibrium is, in addition to $\delta T = 0$, $\delta V = 0$,

$$\delta F = 0. \qquad (19)$$

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[1] This condition further implies that different parts of the system should not be at different temperatures or different pressures, for, otherwise equalisation of temperature and pressure would occur producing an increase of entropy and the system will not be in equilibrium.

[2] There might be other states of equilibrium which may not always satisfy condition (18b), i.e., for them $\delta S \leqq 0$ in general, but there is at least one ***infinitesimal*** variation for which $\delta S > 0$. Such states are in unstable equilibrium and an example of this is the state represented by the point C in Fig. 3, Chap. X. It sometimes happens that for all infinitesimal possible variations $\delta S < 0$, but for some ***finite*** possible variations $\delta S > 0$. Such systems are in metastable equilibrium and examples of these are supersaturated vapours, superheated liquids, supercooled liquids, supersaturated solutions, explosive mixtures, etc. These are easily disturbed by a large enough disturbance. A system is in a state of neutral equilibrium if for some variations $\delta S = 0$ but in general $\delta S < 0$. The triple point is a state of neutral equilibrium.

Of the various states which a system can assume by isothermal processes without doing any external work, only those are stable which correspond to a minimum of free energy.

For *isothermal-isobaric* reactions the condition of equilibrium, in addition to $\delta T = 0$, $\delta p = 0$, is

$$\delta G = 0, \qquad (20)$$

which corresponds to a minimum value of the thermodynamic potential G.

8·10. Thermodynamical Functions, their Properties and Geometrical Representation.—We have already introduced the thermodynamic functions U, H, S, F and G, and discussed their properties. We shall collect them here for the sake of reference. The thermodynamic functions based on the first law are U, the internal energy and H the enthalpy (total heat and heat content are its older names). From the first law $\delta Q = \delta U + p\delta V$, it follows that for changes in a system taking place at constant *volume* the increase in internal energy is simply equal to the heat added, and for changes at constant *pressure* the increase in enthalpy is equal to the heat added to the system, since $\delta Q = \delta(U+pV) = \delta H$. Further[1]

$$\left(\frac{\partial U}{\partial T}\right)_v = C_v; \quad \left(\frac{\partial H}{\partial T}\right)_p = C_p. \qquad (21)$$

From the definition of H, we have

$$dH = dU + pdV + Vdp = TdS + Vdp. \qquad (22)$$

$$\left(\frac{\partial H}{\partial S}\right)_p = T, \quad \left(\frac{\partial H}{\partial p}\right)_s = V, \qquad (23)$$

and

$$H_f - H_i = \int_i^f C_p\, dT.$$

Again from (22) we have for an adiabatic process

$$H_f - H_i = \int_i^f Vdp.$$

The above integral represents the area to the left of an adiabatic curve on a p–V diagram but it does not represent the work done during the process.

The thermodynamic functions based on the second law are S, F, and G. These have been fully discussed in Chap. VI and the foregoing portions of the present chapter. Further in place of dU, we can assume that dF, dG, dH are perfect differentials, and starting from the relevant formula corresponding to equation (2) of Chap. VII and treating it as we did with equation (2), we shall get a whole set of thermodynamic theorems involving F, G and H. The student can easily do this for himself.

---

[1] We can write various analogous formulæ for U and H.

Gibbs also showed the great utility of representing these thermodynamic functions by geometrical surfaces. He took the values of V, S, U as the coordinates x, y, z of a point so that the fundamental equation $U = f(V, S)$ becomes $z = f(x, y)$ representing a thermodynamic surface. Such a thermodynamic surface for water is shown in Fig 2. The various parts of this surface represent the solid, liquid and vapour states of the substance. From the relations $\left(\frac{\partial U}{\partial S}\right)_v = T$; $\left(\frac{\partial U}{\partial V}\right)_s = -p$ it follows that if we draw a plane $S = S_0$ it will cut the surface in a curve whose slope at any point V_0, U_0 gives the pressure p_0 corresponding to the point V_0, S_0, U_0. Similarly the slope of the intersection curve with the plane $V = V_0$ and this surface gives the temperature T_0. Thus the tangent plane at the point V_0, S_0, U_0, contains the two intersecting tangent lines whose slopes give the temperature and pressure at the point. An isothermal-isobaric vaporization will be represented by a straight line in this tangent plane and the triple point will be a plane triangle.

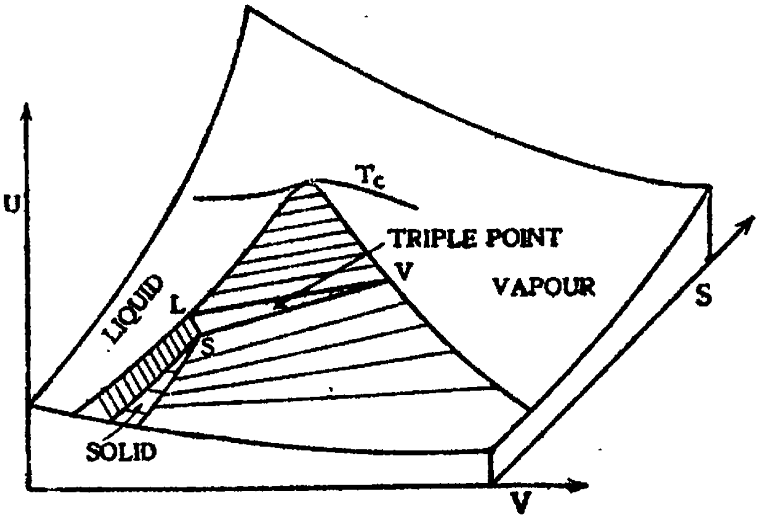

Fig. 2.—Thermodynamic surface for water.

In place of U, Gibbs also used the functions F, G, etc., to construct the thermodynamic surface and discussed geometrically the condition of equilibrium. For stable equilibrium under isothermal-isobaric conditions G is a minimum and therefore the thermodynamic surface must be convex to the tangent plane and above it. For detailed discussion see Gibbs, *Scientific Papers*, Vol. 1.

CHANGE OF PHASE

8·11. Equilibrium between a Liquid and its Vapour.—As an example of the application of the potential G, we shall use it to investigate the equilibrium between a liquid and its vapour or between any two phases of a pure substance. Let us take a closed cylinder containing a liquid in equilibrium with its saturated vapour and kept at a constant temperature and pressure. Since each phase is in equilibrium, the temperature and pressure must be constant throughout the phase, and therefore the thermodynamic quantities V, S, U, G for a phase, as in the case of a simple homogeneous substance, will be equal to their specific values multiplied by the mass in that phase. We have therefore for the whole system

$$G = m_1 g_1 + m_2 g_2,$$

where g_1, g_2 denote the thermodynamic potentials of the saturated liquid and the saturated vapour per unit mass, and m_1, m_2 the masses in these two phases. Further we know from experience[1] that for such a system the temperatures and pressures in the two phases are equal.

Let us produce a virtual change δ in the system consistent with the external conditions. Let this consist in some of the liquid being converted into the vapour state. Evidently this change is isothermal and isobaric, hence we have[2]

$$\delta G = \delta m_l . g_l + \delta m_g . g_g = 0$$

---

[1] We can prove this equality of temperature and pressure for the two phases by assuming the system to be enclosed in a rigid non-conducting enclosure ($\delta V = 0$, $\delta Q = 0$, hence $dU = 0$). Hence for equilibrium $\delta S = 0$. Combining this with the conditions of constraint $\delta V = 0$; $\delta U = 0$, $\delta m = 0$ for the entire system we get $T_l = T_g$, $p_l = p_g$ and $g_l = g_g$. For details see Planck, *Treatise on Thermodynamics* §167—169 or Birtwistle, *Thermodynamics* §57. For the equilibrium to be stable $\delta^2 S$ should be negative.

[2] The process can be conceived of as occurring reversibly, hence we have from (15), $\delta G = 0$.

for equilibrium.[1] Now from the conditions of constraint $\delta m_g = -\delta m_l$, and hence in the equilibrium state

$$g_l = g_g \qquad . \quad . \quad . \quad . \quad . \quad (24)$$

i.e., the thermodynamical potentials per unit mass will have the same value in the two phases.

It is easy to see that the result expressed in (24) is quite general and holds when any two phases of the same substance are in equilibrium. Thus it may be applied to all the three processes of *evaporation*, *fusion* and *sublimation*. We shall now investigate the phenomenon of change of phase in greater detail.

8·12. Effect of Pressure on Boiling Point.—We shall now derive the Clausius-Clapeyron relation by a new method. Let us take an enclosure containing a liquid and its vapour in equilibrium at a certain temperature T, and assume the system to undergo isothermal-isobaric changes only. We have from (24)

$$g_1 = g_2,$$

where g_1, g_2 denote the thermodynamic potentials per unit mass of the liquid and the vapour respectively.

If the temperature be now increased to $T+dT$, then for equilibrium the new thermodynamic potentials must be equal, *i.e.*,

$$g_1 + dg_1 = g_2 + dg_2.$$

Hence
$$dg_1 = dg_2 \qquad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Or
$$\left(\frac{dg_1}{dT}\right)_{\text{sat}} = \left(\frac{dg_2}{dT}\right)_{\text{sat}}. \qquad . \quad . \quad . \quad . \quad . \quad (26)$$

because the condition of saturation is always satisfied. But

$$dg_1 = \left(\frac{\partial g_1}{\partial T}\right)_p dT + \left(\frac{\partial g_1}{\partial p}\right)_T dp, \qquad . \quad . \quad . \quad . \quad . \quad (27)$$

because as the temperature changes, pressure also changes by dp ($p+dp$ being the saturated vapour pressure at $T+dT$). Hence with the help of (16) equation (27) yields

$$\left(\frac{\partial g_1}{\partial T}\right)_{\text{sat}} = -s_1 + v_1\left(\frac{dp}{dT}\right)_{\text{sat}}.$$

---

[1] For the equilibrium to be stable we must also have $\delta^2 G$=some positive quantity, since G has to be minimum. It can be shown that this condition is satisfied if $\delta p/\delta V$ is negative. If $\delta p/\delta V$ is positive this condition is not satisfied and the system will not be in equilibrium. For proof see Planck, *loc. cit.*

Similarly for $(dg_2/dT)_{\text{sat}}$.

Therefore (26) yields

$$-s_1+v_1\frac{dp}{dT} = -s_2+v_2\frac{dp}{dT},$$

or

$$\left(\frac{dp}{dT}\right)_{\text{sat}} = \frac{s_2-s_1}{v_2-v_1} = \frac{L}{T(v_2-v_1)}, \quad . \quad . \quad . \quad (28)$$

where L is the latent heat of vaporization.

This important equation was already deduced in §7·2 and some applications of it were given there. We add two more tables in illustration of (28).

The latent heat of evaporation of water at various temperatures can be calculated from (28) if we know the values of v_2 and $(dp/dT)_{\text{sat}}$ at these temperatures. The values of L so calculated are given in Table 2, together with the observed values. The agreement is seen to be very close.

Table 2.—Latent heat of steam at different temperatures.

t°C.	dp/dT in mm. of Hg	v_2 in c.c.	L (calc.)	L (obs.) Henning
100	27·12	1674	539·5	538·7
110	36·10	1211	533·4	532·1
120	47·16	892·2	526·6	525·3
130	60·60	669·0	520·1	518·2
140	76·67	509·1	512·9	510·9
150	95·66	393·1	505·7	503·8
160	117·7	307·3	497·5	496·6
170	143·4	243·0	489·8	489·4
180	172·7	194·3	481·8	482·2

8·13. Fusion.—Equation (28) also holds in the case of fusion. With its help the change in melting point of any substance with pressure can be easily calculated. The values so calculated, together with the experimentally observed values, for a few metals are given in Table 3.[1] The agreement is fairly satisfactory.

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[1] Taken from Jellinek, *loc. cit.*, Vol. 2, p. 517.

Table 3.—Change in melting point with pressure.

Metal	Melting point °C	Latent heat cal./gm.	v_l-v_g per gm.	δT per 1000 atmos. (calc.)	δT per 1000 atmos. (obs.)
Sn	231·1	14·25	0·003894	+3·34	+3·28
Cd	320·4	13·7	0·00564	+5·91	+6·29
Pb	326·7	5·37	0·003076	+8·32	+8·03
Bi	270·7	12·6	−0·00342	−3·56	−3·55

8·14. Clapeyron's Deduction.—Clausius first gave a rigorous proof of equation (28). The equation was however first deduced by Clapeyron with the help of a Carnot cycle. His deduction, though not quite rigorous, is given below.

Let ABCD, EFGH (Fig. 3) represent two consecutive isothermals at temperatures T and $T+dT$. From F and G draw adiabatics meeting the second isothermal at M and N. We can suppose a unit mass of the substance to be taken through the reversible Carnot cycle FGNM, for instance, by allowing it to expand isothermally along FG, adiabatically along GN and compressing it along NM isothermally and then adiabatically along MF. The substance at F is in the liquid state and at G in the form of vapour. The amount of heat taken during the cycle is therefore $L+dL$ at temperature $T+dT$. Therefore the work done during the cycle is by the second law

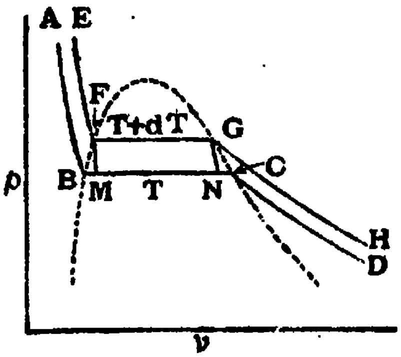

Fig. 3.—Clapeyron's deduction of the Clausius-Clapeyron relation.

$$(L+dL)\left(1-\frac{T}{T+dT}\right)=\frac{LdT}{T}\text{ to the first order.}$$

Again the work done during the cycle = area of the parallelogram FGNM which is in the limit equal to FG multiplied by the perpendicular distance between FG and MN, *i.e.*, dp the increase in pressure due to increase in temperature by dT. Now FG is the change in volume due to evaporation of 1 gram of liquid and is therefore equal to v_2-v_1, where v_2, v_1 denote the specific volumes of the vapour and the liquid respectively. Hence, the area of the cycle is $(v_2-v_1)dp$. Equating the two expressions for the area we get equation (28).

8·15. The Triple Point.—If we plot the saturation value of p against T we get a curve OA (Fig. 4) which satisfies the condition $g_{\text{liq.}} = g_{\text{gas}}$ and the slope is given by

$$\frac{dp}{dT} = \frac{L_2}{T(v_1 - v_2)}, \quad . \quad . \quad . \quad (29)$$

where L_2 denotes the latent heat of vaporisation.

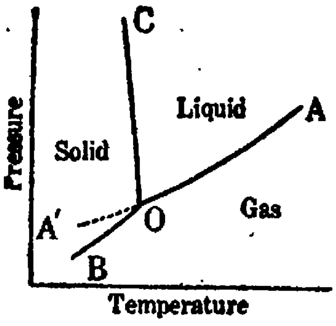

Fig. 4.—Phase diagram of water at low pressures.

To fix our ideas, let us consider the case of water. When the temperature is reduced to 0°C. water freezes and we get ice. But ice has also a definite vapour pressure which has been measured. The vapour pressure curve of ice is obtained from the relation $g_{\text{solid}} = g_{\text{gas}}$ and is represented by OB. The slope of the curve is given by

$$\frac{dp}{dT} = \frac{L_3}{T(v_g - v_s)},$$

where L_3 stands for the latent heat of sublimation.

Similarly we can treat the phenomenon of melting. We have for the phenomenon $g_{\text{solid}} = g_{\text{liq.}}$ and the slope of the curve is given by

$$\frac{dp}{dT} = \frac{L_1}{T(v_l - v_s)},$$

where L_1 denotes the latent heat of fusion. We have discussed this equation on p. 325 and have seen that for ice $dp/dT = 130 \times 10^6$ dynes/deg., *i.e.* the curve is almost vertical. This is represented by OC.

These three curves

$$g_{\text{liq.}} - g_{\text{gas}} = 0 \quad .. \quad \text{(Vaporisation)}$$
$$g_{\text{solid}} - g_{\text{gas}} = 0 \quad .. \quad \text{(Sublimation)}$$
$$g_{\text{solid}} - g_{\text{liq.}} = 0 \quad .. \quad \text{(Fusion)}$$

must meet in a point because by subtracting the first equation from the second we get the third equation. This point of intersection is known as the Triple Point. For water it is nearly but not exactly at 0°C, and can be easily calculated from the consideration that at this point the vapour tension of water is equal to the melting pressure of ice.

At 0°C. the vapour pressure of water is 4·58 mm. while the melting pressure of ice is 760 mm. If we increase the temperature by a very small amount, the vapour pressure does not appreciably change, but the melting pressure changes rapidly. We have to find out the temperature at which the melting pressure reduces to 4·58 mm. From the calculations on p. 325 we have $dT = 0\cdot0075$°C. approx.

The coordinates of the triple point are therefore $T = 0\cdot0075$°C, $p = 4\cdot58$ mm. At this point the three phases (solid, liquid and vapour) coexist.

It was formerly supposed that the curves OA, OB are continuous. It was first proved by Kirchhoff that this is not so, for according to (29)

$$\frac{dp}{dT} \text{ for OA at } 0^\circ = \frac{L_2}{T(v_g - v_l)} = \frac{607 \times 4\cdot18 \times 10^7}{273 \times 21 \times 10^4}$$

$$= 0\cdot337 \text{ mm./degree.}$$

$$\frac{dp}{dT} \text{ for OB at } 0^\circ\text{C} = \frac{687 \times 4\cdot18 \times 10^7}{273 \times 21 \times 10^4} = 0\cdot376 \text{ mm./deg.}$$

since v_g at 0°C $= 21 \times 10^4$ c.c./gm. and v_l, v_s can be neglected.

The dotted curve OA′ is merely the continuation of OA. It represents the vapour pressure of supercooled liquid. At −1°C. we have vapou rpressure of liquid−vapour pressure of solid $= 0\cdot04$ mm. of mercury. This has been verified by the experiments of Holborn, Scheel and Henning.

8·16. Second-Order Phase Transitions.—In §8·11 and 8·12 we worked out the thermodynamics of ordinary phase transitions and derived eqn. (28) which holds for such changes. These are called phase changes of the first order. In these transitions taking place at constant temperature and constant pressure there is a transfer of heat (latent heat) and therefore a change in entropy, as well as a change in volume. By virtue of the defining relations (16) it follows that the first-order derivatives of the Gibbs function with respect to temperature and pressure change discontinuously at the transition point though the Gibbs function is the same in both phases at equilibrium. Thus a phase change of the first order is defined to be one in which the first-order derivatives of the Gibbs function change discontinuously at the transition point. These characteristics of first-order phase transition are graphically represented in Fig. 5 (p. 358) on the left side, and may be mathematically formulated as follows :—

$$g_2 - g_1 = 0. \qquad \ldots\ldots \qquad (50)$$

$$\left(\frac{\partial g_2}{\partial T}\right)_p - \left(\frac{\partial g_1}{\partial T}\right)_p = s_2 - s_1 = \frac{L}{T} \quad . \quad . \quad . \quad (31)$$

$$\left(\frac{\partial g_2}{\partial p}\right)_T - \left(\frac{\partial g_1}{\partial p}\right)_T = v_1 - v_2. \quad . \quad . \quad . \quad . \quad (32)$$

Recent investigations particularly with liquid helium, have brought to light some phenomena where during phase transition no latent heat is evolved and there is no change in volume. This led Ehrenfest[1] to examine the nature of these phase transitions of order, higher than the first. We define a *second-order phase transition* to be one that takes place at constant temperature and pressure *with no change of entropy and volume.* In other words, phase changes of the second order are such that there is no discontinuity but merely a continuous change in the first-order derivatives of the Gibbs function when the substance passes from one phase to the other. Thus in the first-order phase transition the first-order derivatives of the Gibbs function change discontinuously, while in the second-order phase transition, the second-order derivatives of the Gibbs function change discontinuously. These characteristics of second-order phase transition are exhibited graphically in Fig. 5 on the right side and may be mathematically formulated as follows :—

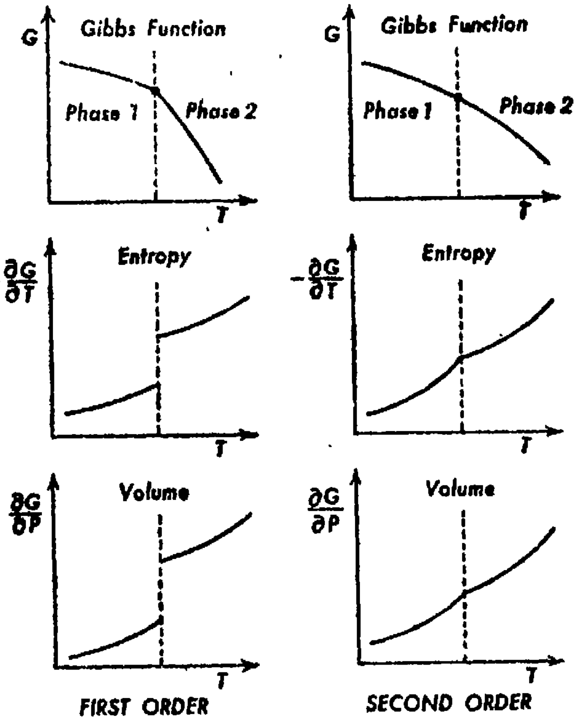

Fig. 5.—Phase transitions of first and second orders.

$$g_2 - g_1 = 0. \quad . \quad . \quad . \quad . \quad . \quad (30)$$

$$\left(\frac{\partial g_2}{\partial T}\right)_p - \left(\frac{\partial g_1}{\partial T}\right)_p = s_2 - s_1 = 0. \quad . \quad . \quad . \quad (33)$$

$$\left(\frac{\partial g_2}{\partial p}\right)_T - \left(\frac{\partial g_1}{\partial p}\right)_T = v_1 - v_2 = 0. \quad . \quad . \quad . \quad (34)$$

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[1] *Leiden Commun.*, No. 75b (1933). See also W. H. Kessom, *Helium*, Elsevier, Amsterdam (1942).

Further, since

$$\left(\frac{c_p}{T}\right) = \left(\frac{\partial s}{\partial T}\right)_p = \frac{\partial}{\partial T}\left[-\left(\frac{\partial g}{\partial T}\right)_p\right]_p = -\left(\frac{\partial^2 g}{\partial T^2}\right)_p,$$

$$\kappa v = -\left(\frac{\partial v}{\partial p}\right)_T = -\frac{\partial}{\partial p}\left[\left(\frac{\partial g}{\partial p}\right)_T\right]_T = -\left(\frac{\partial^2 g}{\partial p^2}\right)_T,$$

$$\alpha v = \left(\frac{\partial v}{\partial T}\right)_p = \frac{\partial}{\partial T}\left[\left(\frac{\partial g}{\partial p}\right)_T\right]_p = -\frac{\partial^2 g}{\partial T \partial p},$$

where κ is the isothermal compressibility and α the volume coefficient of expansion, we have

$$\left(\frac{\partial^2 g_2}{\partial T^2}\right)_p - \left(\frac{\partial^2 g_1}{\partial T^2}\right)_p = \frac{c_{p_1}}{T} - \frac{c_{p_2}}{T}, \quad \ldots \quad (35)$$

$$\left(\frac{\partial^2 g_2}{\partial p^2}\right)_T - \left(\frac{\partial^2 g_1}{\partial p^2}\right)_T = v(\kappa_1 - \kappa_2), \quad \ldots \quad (36)$$

$$\frac{\partial^2 g_2}{\partial T \partial p} - \frac{\partial^2 g_1}{\partial T \partial p} = v(\alpha_2 - \alpha_1). \quad \ldots \quad (37)$$

We can proceed[1] to deduce an equation analogous to the Clausius-Clapeyron equation for a first-order transition. We shall start here from the assumption that $s_1 = s_2$ just as we started with the result $g_1 = g_2$ in §8·12. Hence

$$s_1 = s_2 \quad (\text{at } T,\ p)$$

and

$$s_1 + ds_1 = s_2 + ds_2 \quad (\text{at } T+dT,\ p+dp)$$

$$\therefore\ ds_1 = ds_2$$

But

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp = \frac{c_p}{T}\,dT - \left(\frac{\partial v}{\partial T}\right)_p dp.$$

$$\therefore\ \frac{c_{p_1}}{T}\,dT - v\alpha_1 dp = \frac{c_{p_2}}{T}\,dT - v\alpha_2 dp,$$

since v is the same in both the phases. Hence

$$\frac{dp}{dT} = \frac{c_{p_2} - c_{p_1}}{Tv(\alpha_2 - \alpha_1)}. \quad \ldots \quad (38)$$

Similarly, if we assume $v_1 = v_2$ for the change of the second order we get, as before,

$$dv_1 = dv_2$$

Since

$$dv = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial p}\right)_T dp,$$

we have

$$v\alpha_1\,dT - v\kappa_1\,dp = v\alpha_2\,dT - v\kappa_2\,dp.$$

or

$$\frac{dp}{dT} = \frac{\alpha_2 - \alpha_1}{\kappa_2 - \kappa_1}. \quad \ldots \quad (39)$$

---

[1] A different method of discussing higher-order transitions has been given by Lyppe, *Phys. Rev.*, **69**, 652, 1946.

Equations (38) and (39) are known as Ehrenfests's equations.

The following processes are generally regarded as second-order phase transitions though it is still somewhat doubtful whether they satisfy all or some of the requirements mentioned above :—

(1) Transition of liquid helium I to liquid helium II.

(2) Transition of a superconducting metal to an ordinary conductor in the absence of a magnetic field.

(3) Order-disorder transition in certain alloys and chemical compounds.

(4) Transition at the Curie point of a ferromagnetic to a paramagnetic.

Some of these will be considered in detail later, when the applicability of the Ehrenfest's equations to them will be discussed.

8·17. Thermodynamic Equilibrium of a Heterogeneous System.—When a system consists of only a single homogeneous substance, it is said to consist of only one *phase.* A heterogeneous system is composed of several parts, each of which is homogeneous in itself and is called a phase. We shall now consider the equilibrium of a heterogeneous system in general.

First we shall give a general idea of such systems and explain the terms used in that connection. We have seen that in the case of water at the triple point the system consists of ice, liquid water and water vapour. Each of these different portions is itself quite homogeneous and is separated from others in space by bounding surfaces. These homogeneous (both physically and chemically), physically distinct and mechanically separate portions are called *phases.* A phase need not be chemically pure; in fact a mixture consisting of all kinds of vapours contained in a system forms a single phase, since two vapours are completely miscible and there can exist no surface of separation between them. A mixture of two miscible liquids, a solution, etc., form a single phase. The density, pressure p, temperature T and chemical constitution of a phase remain constant throughout the volume occupied by the phase since it is homogeneous. These are known as 'intensive properties' (intensity factors) of a phase. For the complete description of a phase we must know as many of its intensive properties as are necessary to define its state completely. Hence for this purpose it is enough to specify the temperature, the pressure and the chemical constitution of each phase. The chemical constitution of a phase is specified when the relative proportion of the different chemically defined substances present in the phase is known. Thus all the specific properties (intensive properties) of a phase, such as density, specific heat, etc., depend on the temperature T, pressure p and the chemical constitution of the phase.

In order to specify the chemical constitution of a phase we must state the percentage of each chemically defined substance present in the phase. For this purpose one could state the percentage of each chemical element, (counting the total amount of the element present both in the free and chemically bound state) since we know from the laws of chemistry that under such conditions of specified percentages of the elements at a given temperature and pressure, the percentage of all the possible chemical compounds which can be formed from the chemical elements present is completely determinable. Consider, for example, a gaseous phase consisting of given arbitrary percentages of hydrogen and oxygen (*i.e.*, both varying independently) at a given temperature and pressure. The percentage of H_2O formed (neglecting H_2O_2, O_3, etc., for the sake of simplicity of discussion) is uniquely determined and hence also the chemical constitution of the gaseous phase. Thus the number of independently variable chemical constituents called *components*, is two in this case. By the term 'components' of a·system is meant the number of independently variable chemical species (elements or compounds) by means of which the composition of each phase can be completely specified.

A simple rule to find the number of independent chemical species is first to find the number of chemical elements contained in the system and out of these reject those whose quantity is dependent upon other species. Thus in a solution of NaCl in water we have Na, Cl, H, O elements but the amount of Cl depends upon the amount of Na, that of O upon H. Thus there are only two independent components. There are in general various ways of computing this number of components but it can be shown that the number of independent components as defined above for a system of a given kind is always the same, whatever the manner of grouping the independent components of the elements composing the system. Thus in the salt + water system we may choose the salt and hydrogen, the salt and oxygen, the salt and water or water and Na^+ ion as independent components, but in all cases their number is only two. Thus to some extent there is an arbitrariness as to *which* are the independent components but there is no arbitrariness as to their number. The only conditions governing the choice of independent components are (1) the composition of all phases should be capable of mathematical expression in terms of them; (2) the absolute amounts of these components should be capable of being varied independently of each other in at least one phase. It will be seen from the foregoing discussion that the number of components of a system depends upon the reactions permitted to the system from chemical or physical considerations and may be different for the same system under different conditions. Thus it may be equal to the number of chemical elements as in the example of gaseous mixture of H_2 and O_2 mentioned above, or may be less than the number of chemical elements as for example when H_2O vapour alone is present, for then dissociation can be neglected. The number of components can also be more than the number of chemical elements as for example in an arbitrary mixture of H_2, O_2 and H_2O vapour under such conditions of temperature, pressure, etc., that H_2O is formed or dissociated at an extremely slow rate so that chemical equilibrium can be attained only after a period of time that is exceedingly long as compared to ordinary time intervals. In such a case H_2O may be treated as a practically independent constituent and the number of components thus becomes three.

The number of *degrees of freedom*[1] of a system may be defined as the number of variable factors such as temperature, pressure and relative concentration of the components which can be altered without destroying the nature or the equilibrium of the system. Thus in the case of water at 20°C in equilibrium with its vapour there is one degree of freedom, *viz.*, the temperature. The temperature can be varied independently, the pressure then automatically attains a definite value and cannot be varied independently.

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[1] This term should not be confused with the same term introduced in Chap. III in a different sense.

Having defined the terms phases, components and degrees of freedom, we shall proceed to deduce a relation connecting them—a relation which was first deduced by Willard Gibbs in 1875.

Consider a thermodynamical system of α components in β phases. For the sake of generality we assume that each of the α components is capable of existing in all the β phases.

If the system is subject to isothermal-isobaric changes only, the condition for equilibrium (§8·9) is that the thermodynamic potential **G** is a minimum. Let us assume that the surface energy of the system is negligible so that **G** for the entire system can be expressed as a sum of the thermodynamic potentials of all the phases, *i.e.*,

$$\mathbf{G} = G_1 + G_2 + \ldots . G_\beta. \quad . \quad . \quad . \quad . \quad (40)$$

Let A_{rs} denote any thermodynamic quantity A pertaining to the rth component in the sth phase. The fundamental equation for the homogeneous mixture in the sth phase may be written

$$\mathbf{G} = \mathbf{G}_s\,(T, p, m_{1s}, m_{2s}, \ldots m_{\alpha s}), \quad . \quad . \quad (41)$$

since $\mathbf{G}_s$ depends upon T, p and the masses of the different components in the sth phase. The form of the function will depend upon the special properties of the phase.

We notice that by changing $m_{1s}, m_{2s}, \ldots m_{\alpha s}$ by the same multiplying factor ϵ we do not alter the constitution of our phase (since it depends only on the ratios of the m's) but merely increase the total mass of the phase by the factor ϵ, hence $\mathbf{G}_s$ simply becomes multiplied[1] by the same factor ϵ. This means mathematically that $\mathbf{G}_s$ considered as a function of the α variables $m_{1s}, m_{2s}, \ldots m_{\alpha s}$ is homogeneous of the first degree in the m's. Hence its derivative with respect to any one of the m's as $\partial \mathbf{G}_s/\partial m_{1s}$, $\partial \mathbf{G}_s/\partial m_{2s}$ etc., will be homogeneous of zero degree,[2] that is they depend only upon the ratios of m_{1s}, m_{2s}, etc., and are intensive quantities. Denote these by μ_{1s}, μ_{2s} etc., μ_{1s} being called the '*chemical potential*' of the component 1 in the *s*th phase and is generally referred to mol fraction.[1] Thus μ_{rs} means the increase of the thermodynamic potential per unit addition of the substance 1 to the system the masses of the other constituents remaining constant, and will be a function of T, p and of the ratios of the m's; it might exist even if the substance is not present in that phase. Hence from (41) we obtain

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[1] This is because G is an extensive property (capacity factor) of the phase being additive for phases identical in state. Since U, V, S are extensive properties while T, p, are intensive properties it follows that $G = U + pV - TS$ is also an extensive property.

[2] For proof see Problem 2 at the end of this chapter.

$$\delta G_s = \frac{\partial G_s}{\partial T}\,\delta T + \frac{\partial G_s}{\partial p}\,\delta p + \frac{\partial G_s}{\partial m_{1s}}\,\delta m_{1s} + \frac{\partial G_s}{\partial m_{2s}}\,\delta m_{2s} + \ldots$$

$$= -s\,\delta T + v\,\delta p + \mu_{1s}\,\delta m_{1s} + \mu_{2s}\,\delta m_{2s} + \ldots \qquad . \quad . \quad (42)$$

We had seen that if the system is in equilibrium at a given temperature and pressure, G is minimum. This means that for all infinitesimal virtual changes in the system taking place at constant temperature and pressure

$$\delta G = 0. \qquad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

These changes evidently consist in an infinitesimal quantity of a certain component transforming from one phase to another and so on for all the other components and phases. Substituting the value of G from (40) in (43) and using (42) we obtain

$$\sum_r \sum_s \mu_{rs}\,\delta m_{rs} = 0, \qquad . \quad . \quad . \quad . \quad . \quad (44)$$

as the condition for equilibrium, since T and p are constant.

Now since the total mass of each component remains constant, the system is further subject to the condition of constraint

$$\sum_{s=1}^{s=\beta} \delta m_{rs} = 0. \qquad . \quad . \quad . \quad . \quad . \quad (45)$$

Similar equations will hold for every component of the system. These when expanded may be written as α equations, thus

$$\left.\begin{array}{llll} \delta m_{11}+\delta m_{12}+ & \ldots & +\delta m_{1\beta} = 0 \\ \delta m_{21}+\delta m_{22}+ & \ldots & +\delta m_{2\beta} = 0 \\ \ldots\quad \ldots & \ldots & \ldots \\ \delta m_{\alpha 1}+\delta m_{\alpha 2}+ & \ldots & +\delta m_{\alpha\beta} = 0 \end{array}\right\} \quad . \quad . \quad . \quad (46)$$

We can combine the two conditions expressed by equations (44) and (45) by multiplying the α equations of (46) respectively by $\lambda_1, \lambda_2 \ldots \lambda_\alpha$, and adding to (44). Thus the condition of equilibrium becomes

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[1] When thus referred to, they may be called partial molar thermodynamic potentials.

$$\begin{aligned}&\delta m_{11}(\mu_{11}+\lambda_1)+\delta m_{12}(\mu_{12}+\lambda_1)+\;\ldots\;+\delta m_{1\beta}(\mu_{1}\;+\lambda_1)\\&+\delta m_{21}(\mu_{21}+\lambda_2)+\delta m_{22}(\mu_{22}+\lambda_2)+\;\ldots\;+\delta m_{2\beta}(\mu_{2\beta}+\lambda_2)\\&+\;\;\ldots\;\;\ldots\;\;\ldots\;\;\ldots\;\;\ldots\;\;\ldots\;\;\ldots\;\;\ldots\;=0.\end{aligned}$$

For this to hold, the coefficients of the various infinitesimals δm must separately vanish. Therefore

$$\mu_{11}+\lambda_1=0,\ \mu_{12}+\lambda_1=0;\ \mu_{21}+\lambda_2=0,\ \mu_{22}+\lambda_2=0\ \text{etc.} \quad . \quad (47)$$

Hence

$$\left.\begin{array}{l}\mu_{11}=\mu_{12}=\;\ldots\;=\mu_{1\beta}\\ \mu_{21}=\mu_{22}=\;\ldots\;=\mu_{2\beta}\\ \quad\ldots\;\ldots\;\ldots\\ \mu_{\alpha_1}=\mu_{\alpha_2}=\;\ldots\;=\mu_{\alpha\beta}\end{array}\right\}\quad . \quad . \quad . \quad . \quad (48)$$

i.e., the chemical potential of any component is the same in all phases at equilibrium. These give $\alpha(\beta-1)$ equations of chemical equilibrium and hence $\alpha(\beta-1)$ conditions which govern the internal constitution of phases in the state of equilibrium. We had already seen that μ's are homogeneous of zero degree in m's, *i.e.*, they depend only upon the ratios of m_{11}, m_{12} etc., and not upon the absolute masses, in addition to their dependence on T and p. Equations (48) thus show that the thermodynamic equilibrium depends not on the actual masses of a component in the different phases but only on their ratios. As an illustration it is well-known that the equilibrium between water and water vapour does not depend upon the total quantity of water present.

Now let us see what are the variables of equilibrium, *i. e.*, how many of the variables T, p, etc. must be specified to describe the fact that there is equilibrium. In this heterogeneous system the mass of each component in each phase could be varied. Hence the total number of mass variables is $\alpha\beta$. We have already pointed out above that the nature and type of such an equilibrium does not depend upon the total mass of the components present in a phase but only upon their relative proportion which determines the constitution or composition of the phase, that is, the nature of a phase depends only upon its relative composition (intensive property) and not on its quantity. Hence disregarding mere variations in the quantities of the various phases (which cause no variation in their nature), the nature of each phase is completely specified by T, p and the ratios of the masses of the components in that phase which are $\alpha-1$ in number for each phase. Thus the nature of the system is completely specified by $\beta(\alpha-1)+2$ quantities, T and p being the same for all the phases.[1] Thus the total number of possible variables for the system is $\beta(\alpha-1)+2$. Now since the system is in equilibrium it has to satisfy $\alpha(\beta-1)$ conditions represented by (48). Hence the number of degrees of freedom F of the system, *i.e.*, the number of independent variations permissible to the system, consistent with the maintenance of equilibrium (apart from mere alterations in the amounts of various phases) is given by

$$\mathrm{F} = \beta(\alpha-1) + 2 - \alpha(\beta-1) = \alpha - \beta + 2,$$

or

$$\mathrm{F} = \mathrm{C} - \mathrm{P} + 2, \quad . \quad . \quad . \quad . \quad . \quad (49)$$

C being the number of components, P the number of phases. Or

$$\mathrm{P} + \mathrm{F} = \mathrm{C} + 2.$$

This is the phase rule without chemical reaction.[2]

In the above we have assumed that all components can exist in all the phases. If however certain components are *a priori* excluded from certain phases, the number of total variables possible for the system is reduced but the number of conditions represented by (48) is also reduced by exactly the same amount, and hence (49) remains unaltered.

The number 2 in (49) occurs because we assume that, apart from composition, the state of a phase is completely determined by two intensity factors T and p. If p is immaterial as for systems consisting only of condensed phases, 2 in (49) must be replaced by 1. On the other hand if the nature of the phase undergoes variation with some extra factors such as gravitational energy, etc., the numerical factor in (49) must be correspondingly increased by the number of such extra factors.

APPLICATIONS OF THE PHASE RULE

8·18. One-Component Systems.—From equation (49) which expresses the phase law it will be seen that if the number of phases exceeds the number of components by 2 the degree of freedom is zero, *i.e.*, we cannot vary any of the variables, say the temperature or the pressure, consistently with the condition that all the phases coexist. If we attempt to vary the temperature one of the phases disappears. Such a system is called *non-variant*. As an example we take the case of water at the triple point (Fig. 4). Here the number of components is 1(water), the number of phases is 3 (ice, water, water vapour) and hence the system should have no degree of freedom, *i.e.*, should be non-variant. We know it as an experimental fact that there is a single definite point ($T = +0{\cdot}0074$°C., $p = 4{\cdot}6$ mm.) at which all the three phases are in equilibrium. If we raise the temperature, ice disappears, if we lower the temperature water disappears. Similarly for variations of pressure also.

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[1] This can be proved by considering an isolated system contained in a rigid adiabatic envelope. For proof see Epstein, *Text-book of Thermodynamics* (1937), §40.

[2] If chemical reactions take place, C in (49) must be replaced by C—R—D, where R denotes the number of independent chemical reactions and D the number of such components whose concentrations depend upon other components.

The equation also shows that if a single component is capable of existing in several phases, not more than three phases can under any condition coexist, for otherwise the degree of freedom would become negative. This has been verified by the experiments of Tammann[1] and Bridgman[2] who discovered at least five varieties of ice, but in no case they could obtain equilibrium between more than three phases. In this case six triple points are known. This is very clearly seen in the case of sulphur, where there is only one component and four phases (liquid, gas, rhombic sulphur and monoclinic sulphur). There will be four triple points in this case because four combinations of the phases taking three at a time are possible.

If however the number of phases exceeds the number of components by 1, the degree of freedom is 1. This is called a *monovariant* system. We can vary only one thing independently, say the temperature; the pressure and other variables then automatically assume a definite value which cannot be varied at will. As an example consider the equilibrium between water and water vapour (represented by the line OA in Fig. 4). In this case there are two phases and one component and hence $F = 1$. If we vary the temperature the pressure should assume a definite value, *i.e.*, to every temperature there corresponds a definite vapour pressure. This is quite in accord with experiments.

If the number of phases is equal to the number of components, there will be two degrees of freedom and the system is *divariant*. Examples of this will be found in the next section. Similarly there may be *trivariant* systems and so on.

8·19. Systems with more than one Component.—We have so far illustrated the Phase Rule with a system consisting of a single component. We shall now consider a very simple case of a two-component system—a salt and water. Let us take a dilute solution of a salt in water. The number of phases is two (solution and vapour) and therefore the system is divariant. There are three variables (temperature, pressure and concentration of the solution). Hence by the phase rule we can vary any two of these independently, the third will be automatically fixed. Thus if the temperature and the concentration is varied arbitrarily, the pressure assumes a definite value. In other words a solution of a given concentration at a particular temperature has a fixed and determinate vapour pressure.

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[1] *Ann. d. Physik*, **2**, 1424, 1900.

[2] *Proc. Amer. Acad.*, **47**, 401, 1912.

If the dilute solution is cooled to about 0°C., pure ice begins to separate from it. There are now three phases (ice, solution and vapour) and the system becomes monovariant. Suppose the temperature is varied independently. Then to every temperature there will correspond a definite concentration and a definite vapour pressure.

The behaviour of the system may be represented diagrammatically as in Fig. 6. Here the ordinates represent temperature and the abscissae the concentrations (quantity of salt in 100 c.c. of water). The third variable is the pressure which can be represented along an axis at right angles to the plane of the paper. The change in the state of the system produced by variations of temperature will be represented by a curved surface in space. But we can take p to be fixed (atmospheric pressure) and study the behaviour of the system; then the variable p and the vapour phase fall out of consideration and the graphical representation becomes much simplified. The line AB represents increase in concentration of NH_4Cl caused by gradual cooling due to increasing separation of ice. The solution becomes saturated at B after which both ice and salt separate. If, on the other hand, we start with an excess of NH_4Cl, crystals of NH_4Cl separate due to cooling and we get the curve CB which represents the equilibrium of the phases solid NH_4Cl and homogeneous solution at atmospheric pressure : it is simply the solubility curve of NH_4Cl. The two curves meet in the point B at which solid NH_4Cl, ice and homogeneous solution are in equilibrium at atmospheric pressure. It is a fixed point. If however the three phases were in equilibrium with their own vapour and not the atmospheric pressure we would get some other point corresponding to B in space. This equilibrium point is very little different from B

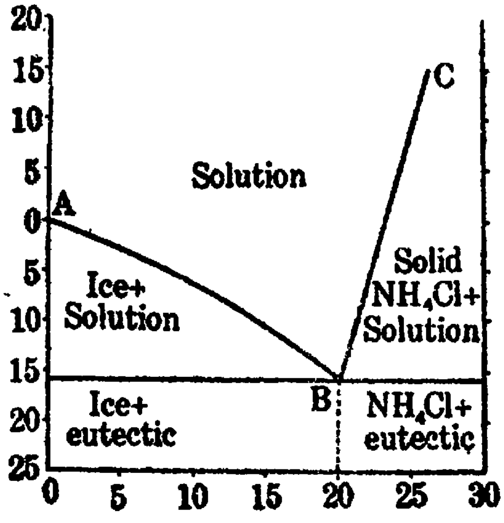

Fig. 6.—Behaviour of the system NH_4Cl and water.

and is called the *quadruple point*, *cryohydric point* or *eutectic point*. It will be seen that it is much lower than the melting point of either component.

At the cryohydric point there are four phases present and the system is non-variant. Thus all the four phases will be in equilibrium at a definite temperature with a definite pressure and a definite concentration of salt in the solution. Therefore any system in which all the four phases are present so alters itself that the cryohydric point is reached. For NaCl and water the equilibrium values are $T = -22°C.$, $p = 0{\cdot}73$ mm., concentration of salt to water is as 36 : 100.

Freezing mixtures.—This explains the principle upon which the action of freezing mixtures depends. When some common salt is mixed with ice, the salt dissolves in the layer of water adhering to the ice. The system thus possesses four phases (salt, solution, ice and vapour) and, as we have seen, it will be in equilibrium only at the cryohydric point. Consequently more of salt dissolves and ice melts and the system alters itself so that the cryohydric point ($T = -22°C.$) is attained. Generally it is done at atmospheric pressure when a fixed point corresponding to B is obtained which is very little different from $-22°C.$

The Phase Rule has various important applications in Physical Chemistry and metallurgy. For these special treatises[1] should be consulted.

PROBLEMS

1. The electromotive force E of a reversible electric cell, as a function of the temperature, is given by $E = 0{\cdot}924 + 1{\cdot}5 \times 10^{-3}\, t + 6{\cdot}1 \times 10^{-6}\, t^2$ volts, t being the temperature in °C. Calculate the heat absorbed by the cell when one coulomb of electricity flows through it isothermally at a temperature of 20°C.

2. If $G\,(\epsilon M_1, \epsilon M_2, \,..\, \epsilon M_n) = \epsilon G\,(M_1, M_2 \ldots M_n)$ prove the Euler theorem

$$M_1 \frac{\partial G}{\partial M_1} + M_2 \frac{\partial G}{\partial M_2} + \ldots M_n \frac{\partial G}{\partial M_n} = G(M_1, M_2, \ldots M_n).$$

[Differentiate the given equation with respect to ϵ and then put $\epsilon = 1$. From the result given above it follows that if G is homogeneous of the first degree in the masses, $\partial G/\partial M$, etc., are homogeneous of zero degree].

3. Show that if U, the internal energy of a phase is equal to

$$U\,(S, V, n_1, n_2 \ldots . n_k),$$

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[1] A. Findlay, *Phase Rule and Its Applications*, Longmans, Green & Co., (1922); C. Desch, *Metallography*, Longmans, Green & Co., (1922); Roozeboom, *Die Heterogene Gleichgewichte*; D. A. Clibbens, *Principles of the Phase Theory*.

where n_k denotes the number of moles of the specie k in that phase, then

$$(a)\ dU = TdS - pdV + \Sigma \mu_k\, dn_k$$

$$(b)\ \ U = TS - pV + \Sigma \mu_k\, n_k$$

where $$\mu_k = \left(\frac{\partial U}{\partial n_k}\right)_{s,\ v,\ \text{other } n\text{'s}}.$$

4. Writing eqn. (42) in terms of molar quantities n_1, $n_2 \ldots$, show that at constant temperature and pressure $G = \sum\limits_i \mu_i n_i$. Hence we have, quite generally, $dG = \Sigma n_i\, d\mu_i + \Sigma \mu_i\, dn_i$. Combining this with eqn. (42) expressed in terms of n's; we get

$$-SdT + Vdp = \Sigma n_i\, d\mu_i,$$

At constant temperature and pressure this reduces to $\Sigma n_i\, d\mu_i = 0$, which is called Gibbs-Duhem relation.

5. Calculate the change of melting point of naphthalene with pressure given that its melting point = 80°C, latent heat of fusion = 4,560 calories per mol., increase in volume on fusion = 18·7 c.c./mol.

6. The transition temperature of mercuric iodide (red→yellow) is 127°C. The latent heat absorbed in the change is 3,150 cal./mol. and the decrease of volume is 5·4 c.c./mol. Calculate dp/dT for the transition point.

BOOKS RECOMMENDED

1. Planck, *Treatise on Thermodynamics.*
2. Gibbs, *Collected Works.*
3. Schottky, Ulich and Wagner, *Thermodynamics.*
4. Epstein, *Text-book of Thermodynamics.*
5. Hoare, *Thermodynamics.*
6. J. H. Keenan, *Thermodynamics*, John Wiley (1941).
7. I. Prigogine and R. Defay, *Chemical Thermodynamics*, Translated by D. H. Everett, Longmans Green & Co., (1954).
8. A. P. Martin, *Principles of Chemical Thermodynamics*, McGraw-Hill (1951).

*CHAPTER IX

STATISTICAL THERMODYNAMICS OF MAXWELL-BOLTZMANN SYSTEMS.

9·1. Introduction.—In the last four chapters we have developed the science of thermodynamics on the basis of two postulates, viz., the first and the second laws of thermodynamics whose validity was taken to be established experimentally. We obtained several relations but could not derive any expression for the specific heat or the equation of state. This is but natural as the methods of thermodynamics hitherto employed, usually called classical thermodynamics, though powerful, have been too general and have not taken into account even the structure of matter.

Another method, viz., the kinetic method, was employed in Chap. III for investigating the behaviour of matter. In this, we made use of the molecular structure of matter, the laws of force between the molecules, their collisions etc., and applied the various dynamical laws. This method is much more complicated and much less general than that of thermodynamics and, in addition, suffers from the disadvantage that the actual force between the molecules is not definitely known.

In this chapter we shall develop a new powerful method, viz., the method of statistical mechanics. *Statistics* can be applied only to such systems which contain a large number of individuals identical in some sense, but distinguishable by means of some property. In *statistical mechanics* the purely statistical method is supplemented by the laws of mechanics which are applied to the individuals composing the system. This method is as powerful and of as wide validity as the method of thermodynamics but assumes, unlike the latter, the concept of molecules and their mutual interaction. Unlike the kinetic theory method, however, it does not require a detailed knowledge of the forces between the molecules or their collisions, etc. and hence the results of statistical mechanics will remain true for whole groups of possible laws of interaction as no detailed calculation of the motion of molecules is made from mechanics. The object of the present chapter is to develop this method of statistical mechanics and obtain therefrom, if possible, a justification of the two laws of thermodynamics which have so far been treated as postulates derived from experience. This method had to be adopted when the various attempts* made in the last century to deduce the second law from purely dynamical principles, such as the principle of Least Action, were all unsuccessful. The deduction of the first law offers no difficulty for it is merely the law of conservation of energy applied to a large assembly of particles. The second law involving the remarkable property of unidirectional change of entropy and the concept of irreversibility cannot be explained from dynamical principles.

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* The student may omit this chapter in the first reading.

Boltzmann was the first to give serious consideration to the cause of these failures. He showed that the second law rested on grounds which are not included in mechanics, but are supplementary to it and he was ultimately able to trace it to the calculus of probabilities.

9·2. Statistical Theory of Heat.—We have already stated in §5·6 that the thermodynamical variables p, V, T ....are the average effects produced by the myriads of molecules of which the substance under consideration is composed. How is this average effect to be calculated? An attempt was made in Chap. III to calculate p and T from the dynamics of the system but various simplifying assumptions had to be made. In a general case however if we want to calculate the average from dynamics we shall have to solve the equations of motion for all the particles with the aid of initial conditions and knowledge of mutual forces between molecules and these are not known. Calculation of the exact average value from dynamics is therefore impossible. We have therefore to take recourse to the statistical theory where we proceed to calculate the average value without investigating the detailed behaviour of the system and finding therefrom the value for each particle. This is rendered possible by the introduction of the concept of *probability* or *chance*—a notion foreign to the dynamical theory. In doing this we ignore the dynamically deterministic behaviour of the particles from the microscopic view-point. We have already defined probability in §3·16 and anybody who has played a game of chance understands its implications. Thus the necessity of working out the statistics of the motion of a large number of particles is easily perceived. As we shall see presently, we arrive in this way at a simple interpretation of the peculiarities of irreversible processes and of the entropy function, the significance of which, unlike that of pressure or temperature, is not at all evident.

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* See Lindsay and Margenau, *Foundations of Physics* (1936), §5·3 (John Wiley and Sons, New York).

To arrive at the idea of entropy, we begin with the problem of conversion of heat energy to mechanical energy which gave us the second law (see §6·2). Though the two forms of energy may be equal in amount they cannot be regarded as equivalent in form. Heat energy consists in the random motion of the constituent molecules which move to and fro in a perfectly *chaotic* way, mostly uninfluenced by their neighbours. When we talk of mechanical work, we want that all these molecules should move with identical velocity in the same direction, and there should be perfect order amongst them. The problem of conversion of heat into mechanical work is thus one of *converting chaotic motion to ordered motion.* It is clear, however, that while a state of ordered motion can easily pass into a disordered state, the reverse process is not so easy of accomplishment. We illustrate the point by an example. Suppose we have a box containing a number of red balls and a number of black balls in two compartments which are open to each other. If the box be now shaken a good number of times, the red and black balls will become *chaotically* distributed. We pass from an ordered state to a disordered state. But it is not possible to realise the reverse process by mere shaking. If we take a box containing red and black balls mixed at random, and shake them a large number of times, there is very little likelihood that the balls will ever assume an arrangement in which the black ones are all ranged on one side, and the red ones on the other. Thus common experience tells us that *the disordered states are the most probable in nature and the ordered* *states are the least probable.* Particles in an assembly left to themselves (as we get in heat motion) are always colliding with each other (corresponding to the shaking process mentioned above) and will therefore spontaneously pass from an ordered (i.e., least probable) state to a state with maximum disorder (most probable) since it is natural to assume that those distributions will actually be realised which have the highest probability. The laws of gases in the equilibrium state, such as the Maxwell's distribution law, should therefore be obtainable from this condition of maximum probability (see §9·5). We thus see that the system has a tendency to change in the direction of increasing probability and the reverse process does not in general take place, i.e., the process is *irreversible.* This is the *statistical analogue of the principle of increase of entropy.* The maximum of entropy corresponds to the maximum disorder, or to the statistical condition of maximum probability. From arguments like these, Boltzmann concluded that there is a functional relation between the thermodynamical function *entropy*, which has always a maximum value in cases of equilibrium, and the maximum probability of distribution of the molecules of the system which we can calculate from statistical treatment of the motion of molecules. This may be mathematically stated in the form $S = f(W)$ where S denotes the entropy and W the probability of the state. For quantitative applications of this relation, the probability W must be precisely defined and the function f determined. This is done in §9·9.

We have seen above how the statistical theory is particularly fitted to explain the concept of irreversibility and the principle of increase of entropy. Its introduction into thermodynamics however has led to a slight modification, rather amplification of the second law itself and brings in its sequel quite a new concept—the *phenomena of fluctuations.* Consider the shaking together of red and black balls already considered. There will be a very small finite probability of the red balls arranging themselves on one side and the black balls on the other, i.e., of evolving order out of disorder. In fact, since in the statistical method we have only probabilities to guide us, there will be a finite probability of the process going either way. It can be shown that the probability of the process occurring in the reverse direction is very small and in general negligible. Thus the second law should be restated thus :— It is *highly probable* that the entropy increases in all naturally occurring processes; decrease of entropy is however not impossible, only it is so much less probable that practically such a state is not found in nature, except in certain unusual circumstances (critical state). This shows that it is possible to observe states other than the usual equilibrium states and the probability of these deviations from equilibrium state (i.e., fluctuations) can be calculated (see §9·6 and 9·3) which is beyond the scope of classical thermodynamics.

Further, the statistical method enables us to think of entropy of non-equilibrium states also defined by the relation $S=f(W)$, though in classical thermodynamics we were accustomed to talk of entropy of equilibrium states only. The statistical theory is also applicable to the great many repetitions of the same experiment and thereby gives us the probability of a certain error being committed during an individual experiment. In view of the great importance of the concept of probability in the statistical theory we shall consider some elementary theorems on the calculus of probabilities.

9·3. Some Elementary Theorems on the Calculus of Probabilities.—Suppose we amuse ourselves by tossing a coin a large number of times and counting the number of times the 'head' or the 'tail' falls uppermost. As explained on p. 131 the probability for each event is exactly $\frac{1}{2}$.

Suppose now we take two coins '1' and '2' and toss them a number of times, and count the following events :—

(1) heads of both fall uppermost .. $a_1 a_2$
(2) tails „ „ „ .. $b_1 b_2$
(3) head of '1' and tail of '2' uppermost .. $a_1 b_2$
(4) tail of '1' and head of '2' uppermost .. $b_1 a_2$

'a' denotes head, 'b' tail. 'a_1' signifies head of '1', b_2 tail of '2'. The possible events are the terms of the product $(a_1+b_1)(a_2+b_2)$.

It is clear that the probability of each event is $\frac{1}{4}$ because all the four events are equally likely. This can also be imagined as follows :—If we toss '1', the probability of our getting the head 'a_1' is $\frac{1}{2}$; if we now toss '2', the probability of getting the head 'a_2' is $\frac{1}{2}$. Thus the probability that in a simultaneous toss of the two coins, we shall be fortunate to have heads of both is $\frac{1}{2}\times\frac{1}{2}=\frac{1}{4}$; in other words, the *probability of a composite event (here a_1, a_2) is the product of the probabilities of the individual and independent component events (i.e., of a_1 and a_2).*

(*i*) WHEN THE COINS CANNOT BE DISTINGUISHED FROM EACH OTHER

In the above example, we have taken the coins to be different from each other, say a silver coin and a copper one. Then the four events can be distinguished from each other. But if the coins are identical, say both identical silver pieces, events (3) and (4) cannot be distinguished from each other. They should be regarded as identical. The possible combinations are now given by the terms of the binomial expression

$$(a+b)^2.$$

The combinations are a^2, ab, b^2.

The chance of getting (a^2) or $(b)^2$ is $\frac{1}{4}$, while the chance of getting ab is $\frac{1}{2}$. It will be seen that the relative chances are in the ratio of the coefficients of the corresponding terms in the binomial expansion.

Extension to 'n' identical coins.—Let us now take 'n' identical coins, and toss them a number of times. The possible combinations are given by the terms of the binomial expansion

$$(a+b)^n.$$

$$i.e.,\ a^n,\ a^{n-1}b, \ldots a^{n-r}\,b^r \ldots .\, b^n.$$

$a^r\,b^s$ denotes that in the throw, we have 'r' heads, and $s=(n-r)$ tails.

It is evident the relative frequency of occurrence of the combination $a^r b^s$ is

$$^nC_r = \frac{n!}{r!\,s!}\ .$$

This can also be seen in the following alternative way. We are asked to choose r coins with 'heads' up, s with 'tails' up, out of a heap of n coins. In how many ways can this be done? Evidently in ^nC_r ways. The *mathematical probability* of the combination $a^r\,b^s$ is

$$W = \frac{^nC_r}{\Sigma\,^nC_r} = \frac{n!}{r!\,s!}\,2^{-n}, \qquad \ldots \qquad (1)$$

since $\Sigma\,^nC_r=(1+1)^n=2^n$; i.e., if we count the combinations in a very large number of throws, we shall find that in the fraction W of the total number of throws, we get the required combination.

(*ii*) COMBINATION POSSESSING THE MAXIMUM PROBABILITY

Let us now calculate which of the $(n+1)$ combinations $a^r\,b^s$ has the maximum probability. We are required to find out the maximum value of ${}^nC_r$. We know from elementary algebra that ${}^nC_r$ is maximum when $r = n/2$. Hence

$$W_{max} = \frac{n\,!}{\left(\frac{n}{2}\,!\right)^2}\,2^{-n} \qquad . \quad . \quad . \quad . \quad . \qquad (2)$$

Let us now compare with W_{max}, the value W_x of a combination in which $r = \frac{n}{2} + x$, $s = \frac{n}{2} - x$ where x is a small number. We have

$$W_x = W_{max}\,\frac{\left(\frac{n}{2}\,!\right)^2}{\left(\frac{n}{2} + x\right)!\,\left(\frac{n}{2} - x\right)!} \qquad . \quad . \quad . \quad . \qquad (3)$$

When n is a very large number, the expression can be reduced to a very simple form by the application of a famous theorem in the theory of numbers, known as the *Stirling's Theorem* after its discoverer (see Note 7). According to this theorem, when n is a very large number, we have $n\,! = \sqrt{2\pi n}\,(n/e)^n$ approximately. Taking logarithm and neglecting terms of the order $\ln n$ we have $\ln n! = n\,(\ln n - 1)$ approximately.

With the aid of this theorem, equation (3), on taking logarithms yields

$$\ln W_x = \ln W_{max} + 2\cdot\frac{n}{2}\left(\ln\frac{n}{2} - 1\right) - \left(\frac{n}{2} + x\right)\left[\ln\left(\frac{n}{2} + x\right) - 1\right]$$
$$-\left(\frac{n}{2} - x\right)\left[\ln\left(\frac{n}{2} - x\right) - 1\right].$$

Using the expansion

$$\ln\left(1 + \frac{2x}{n}\right) = \frac{2x}{n} - \frac{2x^2}{n^2}$$

since $x/n \ll 1$, the above equation yields

$$\ln W_x = \ln W_{max} - \frac{2x^2}{n}.$$

Hence $$W_x = W_{max}\,e^{-2x^2/n} = \frac{n\,!\,2^{-n}}{\left(\frac{n}{2}\,!\right)^2}\,e^{-2x^2/n} \qquad . \quad . \quad . \quad . \qquad (4)$$

which shows that the probability of a large deviation x from the most probable value is vanishingly small.

We have considered here the simple physical experiment of coin tossing but the results deduced above are applicable to any experiment where considerations of probability are applicable such as the phenomenon of random walk (p. 186), problems on molecular dispersion, etc. We can make a formal analogy by associating 'heads' with a positive displacement of the man in the random walk, and 'tails' with a negative displacement. Equation (1) was given by Newton but on account of the occurrence of factorials a more convenient, though approximate, formula was given by Laplace. In this, the more rigorous form of Stirling's theorem is used, viz., $n! = (n/e)^n\sqrt{2\pi n}$, which makes $W_{max} = \sqrt{2/\pi n}$, so that

$$W_x = \sqrt{\frac{2}{\pi n}}\, e^{-2x^2/n} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which is Laplace's formula. This will be in error if n is not large since we have used Stirling's approximation formula. For large x this formula will be in greater error, since the condition $x \ll n/2$ may not then hold, but it is immaterial since W_x itself is then small. Hence (5) is always applicable provided n is large.

(*iii*) THE RANDOM WALK PHENOMENON

Consider the random walk phenomenon, *e.g.*, the aimless walk of a drunken man along a straight course. If 'l' is the length of each step, the distance L traversed corresponding to x is $\left(\frac{n}{2} + x\right) l - \left(\frac{n}{2} - x\right) l$; or $L = 2xl$. Since l is small, L can be treated as a continuous variable, hence $dL = 2l.dx$. Denoting by $W_L\, dL$ the probability for the displacement to lie between L and $L+dL$, we have

$$W_L\, dL = W_x\, dx = W_x\, dL/2l.$$

Hence (5) yields

$$W_L = \frac{1}{l\sqrt{2\pi n}}\, e^{-L^2/2nl^2} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This form of Laplace's equation enables us to calculate the average values readily. From (6) it follows that the average displacement is zero, and the most probable displacement is $1/l\sqrt{2\pi n}$. The mean square displacement is

$$\overline{L^2} = \int_{-\infty}^{\infty} L^2\, W_L\, dL = nl^2, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

from (6). The infinite limits have been used for the sake of mathematical simplicity. The root-mean-square deviation of L from its average value, usually called ***standard deviation***, is

$$\lambda = \left[\overline{(L-\bar{L})^2}\right]^{\frac{1}{2}} = \left[\overline{L^2} - 2\bar{L}^2 + \bar{L}^2\right]^{\frac{1}{2}} = \left[\overline{L^2}\right]^{\frac{1}{2}}$$

since $\bar{L}=0$. Hence from (7), $\lambda = l\sqrt{n}$, and (6) can be written in the form

$$W_L = \frac{1}{\lambda\sqrt{2\pi}}\,e^{-L^2/2\lambda^2}. \qquad (8)$$

Equation (8) is of great importance in the interpretation of the results of quantitative experiments. We know that when an experiment is repeated under (apparently) identical conditions, the numerical result of the measurement will rarely be identical. What is the correct value then ? It is most natural to assume that the correct value is the average or arithmetic mean of the observed results. This will be so provided there are no *systematic* errors (i.e. error due to improper manipulation or neglect of some factors); the errors are assumed to be only *accidental* being governed by chance alone. The statistical theory can be applied to these accidental errors. It can be shown that the probability of an error L is given by (8), where the constant $\sqrt{1/2\lambda^2}$ is called the "*measure of precision*" and was denoted by $\sqrt{K}$ on p. 135. Equation (8) is usually known as the *normal distribution* law or *Gaussian Error Law*.

(iv) EXTENSION TO PARTICLES HAVING LARGE NUMBER OF STATES

Instead of taking coins as in (i) and (ii) above which have only two states, we can take other bodies possessing a large number of *possible states*. An example is afforded in the game of dice. Each die has six sides which we may denote by a, b, c, d, e, f. What is the probability that if we toss a large number n of dice, we shall get a combination

$$a^{n_1}\; b^{n_2}\; c^{n_3}\; d^{n_4}\; e^{n_5}\; f^{n_6}$$

i.e., n_1 dice fall with face 'a' up, n_2 with face 'b' up, etc.

We obtain by arguments similar to those used above that P, the *possibility number* for this combination is

$$P_x = \frac{n\,!}{n_1!\; n_2!\; n_3!\; n_4!\; n_5!\; n_6!}. \qquad (9)$$

The mathematical probability for the combination is

$$W_x = \frac{P_x}{\Sigma P_x} = \frac{n\,!}{\prod n_r\,!}\,6^{-n}.$$

Now we shall pass on to a more general case. Let us assume that each particle can exist in any one of the states denoted by the symbols

$$a_1,\ a_2,\ a_3,\ a_4, \ldots .$$

To visualize matters, let us take a fresh illustration. We take a board with p square cells arranged side by side and let us throw into these cells a number n of balls from a great distance. Let us suppose that n_1 balls are found within the cell a_1, n_2 in a_2, etc.

The possible combinations are found by giving n_1, n_2 ...all possible values subject to the condition $\sum n_r = N$. Let us find out the "possibility number" of the above combination. This is $P_x = N!/\prod n_r!$ and the mathematical probability

$$W = \frac{P_x}{\sum P_x} = \frac{N!}{\prod n_r!} p^{-N}$$

where p is the total number of cells.

9·4. Statistics of the Motion of a Molecular System.—

We shall now resume the problem of working out the statistics of the motion of an assembly of weakly interacting, similar particles, say that constituting a perfect monatomic gas. But the argument that follows holds good for any dynamical system, e.g., a system of oscillators in a blackbody chamber. It is applicable even to non-mechanical systems such as the distribution of independent objects, not at all moving, in a set of boxes. There are various ways of attacking this problem but we shall adopt here the method of statistical distribution[1] due to Maxwell and Boltzmann which is simplest and historically the oldest.

The dynamical condition of a particle[2] is determined by its positional co-ordinates, x, y, z and its velocity co-ordinates or rather momenta $p_x = mu_x$, $p_y = mu_y$, $p_z = mu_z$ where u_x, u_y, u_z are the components of the velocity of the particle. The specification of these values for all the particles defines the "microscopic state" of the system. The problem before us is now to find out how many particles occupy very nearly the same position, and have nearly the same velocity components. Two particles cannot evidently occupy the same point in space. We therefore consider the particles having their co-ordinates between x, $x+dx$, y, $y+dy$, z, $z+dz$. These again may have any velocity components lying between 0 and ∞ but we are concerned only with those having their momenta components between p_x, $p_x + dp_x$, p_y, $p_y + dp_y$ and p_z, $p_z + dp_z$. Thus we define an element of hyperspace $dx dp_x\, dy dp_y\, dz dp_z$ to which we assign n_r particles. In the case of linear harmonic oscillators as well, we can assign n_r to a similar element of hyperspace which will be in this case two-dimensional. For a monatomic gas this hyperspace, called *molecular phase-space* or *μ-space*, is six-dimensional. We can map out completely the dynamical state of the gas by imagining a number of small cells of equal size extending throughout the entire phase-space and thus embracing the whole volume, and the whole range of momenta between 0 and infinity. Let the cells be denoted by $a_0, a_1, a_2, \ldots\ldots a_r, \ldots$ the cell a_r containing molecules each having a definite amount of energy[1] ϵ_r and let us distribute the N indistinguishable molecules among these cells. Consider the distribution of the molecules with respect to their energy such that n_0 molecules are found in a_0, n_1 in a_1, n_r in a_r and so on. The cells now correspond to the sides of the dice. The possibility number[2] of realising this distribution, which may be distinguished by the suffix x, is from (9)

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[1] This method is essentially non-mechanical and therefore possesses the advantage that it can be easily carried over into wave mechanics but suffers from the disadvantage that it operates only with free particles and neglects mutual interactions which are generally present.

[2] For polyatomic molecules more co-ordinates will be necessary to specify rotation and vibration.

$$P_x = \frac{N!}{\prod n_r!} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

and
$$W_x = \frac{P_x}{\Sigma P_x} = P_x\,(p)^{-N}.$$

where p is the total number of cells. In deducing (10) we assumed that a molecule was as likely to be in one cell as in the other, i.e., the cells have the same á priori probability[1]. This is because the cells are of equal size. This result is evident if the cells were like boxes in the ordinary three-dimensional space. The same result can however be proved for cells in the 6-dimensional phase-space (see Liouville's Theorem—Note 8). Hence the probability of the distribution is proportional to P_x .

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[1] Variation of energy with variation of position inside the cell is here neglected.

[2] This is also called the number of '*complexions*' or the number of microscopic states all of which give rise to the same macroscopic state and are simply obtained by interchanging pairs of entirely similar molecules which were assigned to different cells of the μ-space, since for a macroscopic description the distribution of N molecules in the μ-space and not their identity is significant. This gives us P_x [expressed by (10)] as the number of possible arrangements of the N molecules for the distribution $n_1, n_2, \ldots$, or the number of complexions or microscopic states pertaining to this distribution. Since in dynamics the concept of probability plays no part, we can assume that every dynamical or microscopic state is equally probable, provided it can occur at all (attempt is sometimes made to prove it from the so-called *ergodic hypothesis* but it should be considered as a postulate). It follows therefore that the probability of a macroscopic state is proportional to the number of complexions. It is further assumed that the probability in this frequency sense is identical with probability in the sense of likelihood of finding that a system is in the condition concerned.

We have further

$$N = n_0 + n_1 + n_2 + \ldots + n_r + \ldots \qquad (11)$$

and the total kinetic energy

$$U = n_0 \epsilon_0 + n_1 \epsilon_1 + \ldots + n_r \epsilon_r + \ldots \qquad (12)$$

Dynamically any distribution which satisfies the conditions (11) and (12) is possible, but we know that all the states are not equally probable. For example, we may imagine that certain parts of the volume contain no molecule at all and all the molecules crowd into one corner of the volume. Though this is dynamically possible, we know as a matter of experience that such a state is never found to occur, or the probability of its occurrence is infinitely small. The same may be said of a fancied distribution in which all particles move with equal energy; the probability of such an occurrence will be infinitely small. We now consider in the next section the case in which the probability is maximum.

9·5. State of Maximum Probability for an Assembly of Particles.

—The state of maximum probability of an assembly of particles is obtained by making W or P a maximum, subject to the conditions imposed by (11) and (12). We proceed now to work out this analysis.

In this argument we have assumed that the interchange of two similar molecules produces a significant change in the dynamical or microscopic state of the system. This implies the possibility, at least in principle, of keeping a continuous observation on the system which would enable us to know whether two similar molecules exchange their roles or not. This is possible in classical mechanics but not in quantum mechanics where we lose all knowledge of distinction between two similar molecules when they suffer a sufficiently close encounter with each other. This latter case will be considered in Chap. XVII.

[1] If the cells have different à priori probabilities g_r (say, on account of their sizes being different) expression (10) for P_x must be multiplied by $\prod g_r^{n_r}$ to give W_x because the probability for n_r particles to be in the a_r cell becomes $g_r^{n_r}$ time greater In the case considered all the g's are equal, being given by $1/p$.

We have from (10), using Stirling's theorem[1] as before and taking logarithms

$$ln\ P = N\,(ln\ N-1) - \Sigma\, n_r\,(ln\ n_r-1).$$

Putting $\omega_r = n_r/N$, we get

$$ln\ P = N\,(ln\ N-1) - \Sigma\, N\omega_r\,(ln\ N + ln\ \omega_r - 1)$$

$$= -N\ \Sigma\ \omega_r\, ln\ \omega_r\,. \qquad . \quad . \quad . \quad . \quad (13)$$

For the condition of maximum probability, we have[2]

$$\delta\, ln\, P = -N\ \Sigma\ (1 + ln\ \omega_r)\ \delta\omega_r = 0. \qquad . \quad . \quad (14)$$

We have also from (11) and (12)

$$\Sigma\, \omega_r = 1, \text{ and } \Sigma\, \epsilon_r\omega_r = U/N.$$

Since the system is isolated, its total energy as well as the number of molecules is fixed. Hence

$$\delta N = N\Sigma\, \delta\omega_r = 0,\ \ \delta U = N\Sigma\, \delta\omega_r\ \epsilon_r = 0. \quad . \quad . \quad . \quad (15)$$

Combining (14) and (15) by the method of undetermined multipliers, we have

$$\Sigma\ (ln\ \omega_r + \lambda + \beta\epsilon_r)\ \delta\omega_r = 0.$$

Since the variations are quite arbitrary, we have

$$ln\ \omega_r + \lambda + \beta\epsilon_r = 0, \text{ or } \omega_r = \frac{1}{f}e^{-\beta\epsilon_r} \qquad . \quad . \quad . \quad . \quad (16)$$

where f and β are constants. β is called the *modulus of distribution,* and ω_r is the *distribution function.* It expresses the proportion of molecules having the energy ϵ_r. The number of particles having energy ϵ_r is equal to

$$N\omega_r = \frac{N}{f}e^{-\beta\epsilon_r} \qquad . \quad . \quad . \quad . \quad . \quad . \quad (16a)$$

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[1] This theorem is applicable for large n. In a gas the number of molecules is very large and therefore most of the n_r's will be large. But it is quite possible that for some cells n_r may be small. The use of Stirling's theorem for these, though not justified, will produce only a small error in (13) as the contribution itself of these terms to the whole sum in (13) is very small. Alternatively, we might assume that only the large n_r's are varied.

[2] The numbers n_r being large, the variations δn_r, $\delta\omega_r$ can be treated as continuous variables and the calculus of variations applied. The resulting equation (16a) will be applicable only to such states for which n_r is large.

From its mode of derivation it follows that the number of particles n_r will be given by (16a) provided n_r is large as is actually the case for gases.

It will be shown later that $\beta = 1/kT$. Thus (16a) is identical with Maxwell-Boltzmann law of distribution (§3·25) which includes Maxwell's law as a special case. Thus we see that the *most probable* distribution is that of Maxwell.

9·6. The Normal Distribution.—We will now show that the most probable distribution is the actual or normal distribution. To prove this, let us find the probability of a small deviation $\delta\omega_r$ from the most probable value of ω_r as given by (14) or (16) for which the first order terms in $\delta \ ln \ P$ vanish. Using (13) the change in $ln \ P$ from its maximum value is

$$\triangle \, ln \, P = -N \Sigma (\omega_r + \triangle\omega_r) \, ln \, (\omega_r + \triangle\omega_r) + N \Sigma \omega_r \, ln \, \omega_r \, .$$

But $$ln \, (\omega_r + \triangle\omega_r) = ln \, \omega_r + \frac{\triangle\omega_r}{\omega_r} - \tfrac{1}{2}\left(\frac{\triangle\omega_r}{\omega_r}\right)^2 \text{ approx.}$$

$$\therefore \ \triangle \, ln \, P = -\frac{N}{2} \Sigma \omega_r (\triangle\omega_r/\omega_r)^2 = -\tfrac{1}{2} \Sigma n_r (\triangle n_r/n_r)^2 \quad . \quad (17)$$

from (14) and the condition $\Sigma \triangle\omega_r = 0$. From (11) and (12) it follows that if both N and U are increased towards infinity at the same relative rate each of the n_r is increased in the same ratio. Hence for given fixed value of $\triangle n_r/n_r$, $\triangle \, ln \, P \to -\infty$ as the molecules become more numerous which implies that deviations from the most probable value occur only very rarely if the total number of molecules is large.

9·7. Introduction of Temperature.—If there are molecules of more than one kind present in the system such as a mixture of nitrogen and argon gases, we would get by proceeding as in §9·4 and §9·5 formulæ similar to (16a) for each gas in the state of equilibrium with the same distribution modulus β but with a different N/f. Since the two gases in the state of equilibrium must have the same temperature, the equality of β must imply the equality of temperature, or in other words $\beta = f(T)$.

We shall now introduce temperature quantitatively into these statistical considerations. There are two methods in general use :—(1) By using the second law of thermodynamics which serves to define temperature, (2) by making use of the equation of state of a perfect gas (perfect gas thermometer). We shall adopt here the latter method and use the former to yield a statistical equivalent of the second law itself.

Equation (16) gives us the probability that a molecule will lie in the cell of energy ϵ_r. Since the molecule is equally likely to be in any part of the cell, the probability that the molecule lies in any elementary phase volume

$$dq_1 \, . \, dq_2 \, . \, dq_3 \, . \, dp_1 \, . \, dp_2 \, . \, dp_3 = dg,$$

inside the cell is given by $P\,(q,\,p)\;dg$ where

$$P\,(q,p).\,dg = \frac{1}{f} e^{-\beta\epsilon_r} \; \frac{dq_1.\, dq_2.\, dq_3.\, dp_1.\, dp_2.\, dp_3}{g}, \qquad (18)$$

g being the volume of the cell. Equation (18) expresses the distribution law in the differential form where the constant $1/fg$ may be replaced by a new constant C_1. The constants C_1 and β may be evaluated in the same manner as in §3·18.

We have from (18),

$$1 = \int \ldots\ldots \int C_1 \; e^{-\frac{\beta}{2m}(p_1^2+p_2^2+p_3^2)} \; dq_1.\, dq_2.\, dq_3.\, dp_1.\, dp_2.\, dp_3.$$

$$= C_1 \left(\sqrt{2\pi m/\beta}\right)^3 V, \qquad (19)$$

since $\iiint dq_1.\, dq_2.\, dq_3$ over the entire container is simply the volume V of the container, and the limits for the p's extend from $-\infty$ to $+\infty$. The molecules contained in the volume p_1/m strike unit area of the wall perpendicular to q_1 axis in unit time and exert the momentum $2p_1$ per molecule since they suffer elastic collision. Hence the pressure p exerted by the molecules is given by

$$p = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{0}^{\infty} \frac{p_1}{m} . \; \frac{NC_1}{V} e^{-\frac{\beta}{2m}(p_1^2+p_2^2+p_3^2)} \, 2p_1 \, V dp_1 \, dp_2 \, dp_3.$$

$$= \frac{N}{\beta V}, \qquad (20)$$

after evaluation and substitution of the value of C_1 from (19). Using the perfect gas relation $p = NkT/V$, (20) gives

$$\beta = 1/kT. \qquad (21)$$

9·8. Statistical Analogues of the Laws of Thermodynamics.—In order to apply thermodynamics to the foregoing statistical system, we must subject the system to a small thermodynamic process which is assumed to be carried out so slowly that it is reversible. During such a process work may be done on the system and heat may also enter the system. Energy in the form of work enters the system when external forces, averaged over irregular molecular fluctuations, act on the system producing a change in the potential energy. On the other hand the irregular forces over and above this constant average force, which we may call thermal forces, impart energy to the system and this constitutes the heat absorbed by the system.

The internal energy U of the system is given by $U = \Sigma\, n_r\, \epsilon_r$. Hence the change in internal energy is

$$dU = \sum_r (n_r .\, d\epsilon_r + \epsilon_r .\, dn_r). \quad . \quad . \quad . \quad (22)$$

Now suppose that the thermal forces are absent and work is done on the system by a change in the external coordinates λ_1, λ_2 such as changes in the position of the wall or piston etc. The resulting change in energy is $dU = +\sum_r \sum_j n_r \frac{d\epsilon_r}{d\lambda_j} d\lambda_j$ $= \sum_r n_r\, d\epsilon_r$ since $-d\epsilon_r/d\lambda_j$ represents the force brought to act on the particle, $d\epsilon_r$ being the change in the energy of the cell. The work-forces produce no net contribution to the second term in (22) since the changes in n_r are governed by the dynamical motion of the system and are not affected by changes in λ. The work dW done by the system is the negative of the work done on the system. Hence

$$\delta W = - \sum_r n_r\, d\epsilon_r. \quad . \quad . \quad . \quad . \quad (23)$$

Now let the heat δQ be applied to the system so that thermal forces also begin to act. The change in energy dU will now be given by the general expression (22). The second term arises from the thermal forces, i.e., the irregular forces over and above the constant forces and for these ϵ_r is constant. The change consists in a shifting of the molecules from one cell to another accompanied by an absorption of heat. In (15) we had put

$\Sigma \epsilon_r \, dn_r = 0$ because that referred to an irreversible approach to equilibrium but here the case is different. This refers to a change from one equilibrium state to another equilibrium state of different energy produced by absorption of heat. Assuming that the application of heat δQ does not affect the work done by the system to the first order which is still given by (23) we have from the principle of conservation of energy

$$\delta Q = dU + dW = \sum_r \epsilon_r . \, dn_r \qquad . \quad . \quad . \quad (24)$$

from (22) and (23). But from (16a)

$$\sum_r \epsilon_r . \, dn_r = \frac{1}{\beta} \sum_r \left(ln \, \frac{N}{f} - ln \; n_r \right) dn_r$$

$$= - \frac{1}{\beta} \Sigma \; ln \; n_r . \, dn_r, \qquad . \quad . \quad . \quad (25)$$

since $\Sigma \; dn_r = 0$. Again from (13), we have

$$d \; ln \; P = - N \Sigma \; (1 + ln \; \omega_r) \; d\omega_r = - \Sigma (1 - ln \; N + ln \; n_r) \; dn_r$$

$$= - \Sigma \, ln \; n_r \, dn_r . \qquad . \quad . \quad . \quad . \quad (26)$$

If (25) and (26) are to correspond to the same distribution, P must refer to the most probable distribution P_m since (25) refers to that distribution.

Hence combining (24), (25) and (26), we get

$$\delta Q = \frac{1}{\beta} \; d \; ln \; P_m, \qquad . \quad . \quad . \quad . \quad (27)$$

as the statistical analogue of the first law of thermodynamics. Substituting the value of $\beta = 1/kT$ from (21), equation (27) yields the relation

$$\frac{\delta Q}{T} = dS = k . \; d \; ln \; P_m \qquad . \quad . \quad . \quad . \quad (28)$$

as the statistical analogue of the second law for a system obeying the canonical distribution (16a). Integrating (28) we get

$$S = k \, ln \; P_m + C' \qquad . \quad . \quad . \quad . \quad (29)$$

as the relation connecting the thermodynamic quantity, entropy S, with the statistical quantity P_m, the maximum number of possible arrangements or complexions corresponding to that microscopic state. Evidently P_m is proportional to the probability of the state; Planck calls P_m the '*thermodynamic probability*' of the state. C' is an arbitrary integration constant whose value cannot be determined from classical statistics. Equation (29) is a famous relation connecting entropy with the maximum probability of the state and was first given by Boltzmann, but he deduced it intuitively in a more direct manner. Before proceeding further, we shall take up Boltzmann's deduction of this theorem and some of its applications.

9·9. Boltzmann's relation between Entropy and Probability.—We saw in §9·2 how Boltzmann discovered a connecting link between entropy and probability. He started from the simple idea that any system so alters itself that in the state of thermodynamical equilibrium its entropy is maximum. On the other hand, statistically speaking, the system will alter in the direction of increasing probability, which will thus attain a maximum value in the equilibrium state. Thus Boltzmann concluded that entropy is a function of the probability of the state and so linked up thermodynamics with statistics.

Let us therefore assume that $S = f(W)$, where W is the probability of the state. To find out the nature of the function, we observe that while the *entropy function is additive, probability is multiplicative.* If we have two independent systems A and B with the entropies S_1 and S_2, the entropy of the combined[1] system consisting of A and B is S_1+S_2. But if the probability of A be W_1, and of B be W_2, the probability of the combined system is $W_1 \times W_2$. Hence we have

$$S_1 + S_2 = f(W_1) + f(W_2) = f(W_1 W_2).$$

This functional equation is satisfied by the relation (*vide* Note 9)

$$S = k \ln W + C. \quad . \quad . \quad . \quad . \quad (30)$$

This relation was given by Boltzmann but he left the constants k and C undetermined. Planck later introduced P, the thermodynamic probability in place of W since the two are proportional, and assumed the constant C to be zero. Thus he assumed $S = k \ln P$ and calculated with its help the absolute value of entropy. This is however not justified as we shall see later.

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[1] Combined system does not mean that we are mixing up the two systems. They are still apart and not allowed to interact.

9·10. Some Ready Applications of Boltzmann's Law—Law of Perfect Gases.—Let us calculate the probability that a particle finds itself within a fractional volume V when a large volume V_1 is available to it. The probability is clearly V/V_1. The probability of another particle being confined within it is also V/V_1 and the probability of both particles being simultaneously confined in volume V is $(V/V_1)^2$. Proceeding in this way we find that the probability W of all the molecules lying in the space V is $(V/V_1)^N$. Hence from (30)

$$S = kN\,[ln\ V - ln\ V_1] + C. \quad . \quad . \quad . \quad (31)$$

From the second law $dU + pdV = TdS$, we have for a perfect gas, since $(\partial U/\partial V)_T = 0$,

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_T = \frac{Nk}{V}$$

from (31). Hence

$$pV = NkT, \quad . \quad . \quad . \quad . \quad . \quad (32)$$

which is the Boyle-Charles-Avogadro Law. We find that the k of (30) is the same as Boltzmann's gas constant R/N.

Imperfect Gases. Deduction of van der Waals' Equation of State.

In the above deduction, it was implicitly assumed that the space occupied by the molecules was negligible. Let us now suppose that a molecule is a sphere having the radius r. Then when a particle takes up a position within the volume V, no other particle can have its centre within a distance $2r$ from the centre of the first; hence the volume $4\pi/3 . (2r)^3 = 8$ times the molecular volume $= \beta$ is not available to other molecules. Hence for the first molecule the probability is V/V_1, but for the second it is $\frac{V-\beta}{V_1-\beta}$, for the third $\frac{V-2\beta}{V_1-2\beta}$ and for the r-th it is $\frac{V-\overline{r-1}\beta}{V_1-\overline{r-1}\beta}$. Hence neglecting V_1 terms (for they would cancel on differentiation with respect to V later), we find that the probability that N molecules will be confined within the volume V is

$$W = V(V-\beta)(V-2\beta)\ldots(V-\overline{N-1}\,\beta) = V^N \prod_r \left(1 - \frac{r-1}{V}\beta\right)$$

$$= V^N\left(1 - \frac{Nb}{V}\right) \text{ approx.,} \quad . \quad . \quad . \quad (33)$$

where $b = N\beta/2 = 4$ times gram-molecular volume. Hence

$$S = k\,ln\,W = k\,ln\left[V^N\left(1 - \frac{Nb}{V}\right)\right]. \quad . \quad . \quad . \quad (34)$$

From the relation (34) we get

$$\frac{p}{T}=\left(\frac{\partial S}{\partial V}\right)_T=\frac{kN}{V}\left(1+\frac{b}{V}\right)=\frac{kN}{V-b}\text{ approx.,} \qquad (35)$$

provided $(\partial U/\partial V)_T=0$, i.e., the molecules do not exert any force on one another.

A rigorous calculation shows that

$$p=-\frac{RT}{2b}\,ln\,\frac{V-2b}{V}, \qquad (36)$$

from which formula (35) comes out as the second approximation.

9·11. Value of Entropy.

9·11. Value of Entropy.—From equation (29) or follows that we can write quite generally

$$S=k\,ln\,P_m+C',$$

where P_m denotes the maximum (thermodynamic) probability, i.e., the probability of the equilibrium state, and is given by (13) subject to (16). Substituting for P_m we have

$$\begin{aligned}S&=-kN\sum\omega_r\,ln\,\omega_r+C'\\&=-kN\sum\omega_r\left(ln\frac{1}{f}-\beta\epsilon_r\right)+C'\\&=kN.\,ln\,f+U/T+C', \qquad (37)\end{aligned}$$

where $f=\Sigma\, e^{-\epsilon_r/kT}$. The quantity f is called the *partition function* or 'sum-over-states' or simply 'state-sum' (*Zustandssumme* in German) and its evaluation from mechanics is necessary for a determination of the thermodynamic behaviour of the system.

To evaluate the partition function f we replace for the sake of mathematical convenience, the summation by a triple integration as explained in §9·7 and further assume that the limits for p_1, p_2, p_3 are $-\infty$ and $+\infty$ respectively. Actually there will be finite maximum and minimum values of the momentum components but on account of the exponential nature of the integrand the replacement of these limits by $+\infty$ and $-\infty$ will be a very close approximation. Proceeding as in §9·7 we have from (19), since $C_1=1/fg$ and $\beta=1/kT$,

$$f=\frac{V}{g}\,(2\pi mkT)^{3/2}. \qquad (38)$$

In deducing this we have assumed that the volume of the cells in the molecular phase space remains constant during the motion of molecules. This follows from a famous theorem due to Liouville known as the "*Principle of Conservation of Extension in Phase*" which states that

$$\frac{d}{dt}(\Pi\, dp.\, dq) = 0, \quad \ldots \quad (39)$$

where p and q are momenta and position coordinates respectively. The product extends over all the degrees of freedom of a particle. For proof of this important theorem see Note 8. It will be observed that Liouville's theorem only says that the size of the cell in the phase space is constant; it tells us nothing about its value. In fact classical statistical mechanics is quite incapable of determining the value of g; it can have any value whatsoever.

Let us substitute the value of f from (38) in (37). We get

$$S = Nk\, ln \frac{V}{g}(2\pi mkT)^{3/2} + \frac{3}{2}Nk + C', \quad \ldots \quad (40)$$

since for a classical perfect gas $U = \frac{3}{2}NkT$. It can be shown in various ways that this equation is not correct. For if both N and V are doubled, the entropy is not doubled according to this equation, as it should be, from equation (26) of Chap. VI. To secure this or, in other words, to make entropy behave as an extensive property, we can assign a suitable value to the hitherto undefined arbitrary constant C'. Let us put $C' = -k\, ln\, N! + S_0$. Looking back to equation (10) we see that this amounts to a division of P by $N!$ This was first pointed out by Sackur and the correct explanation for this can be given only from quantum mechanics (Chap. XVII). $P/N!$ may be called the 'effective' statistical probability and it is this probability which must be used in calculating entropy from (29). Substituting this value of C' in (40) we get

$$S = Nk\, ln \frac{V}{Ng}(2\pi mkT)^{3/2} + \frac{5}{2}Nk + S_0 \quad \ldots \quad (41)$$

This expression gives the value of entropy of a perfect monatomic gas. It is thus seen that classical statistical mechanics is unable to determine the integration constant occurring in equation (26) of Chap. VI, since the value of g and S_0 is not known here.

9·12. Gibbs' Representative Ensemble Method.—So far we have developed statistical mechanics by the Maxwell-Boltzmann-Planck method. The method has several limitations. In the first place it is applicable only to an ideal gas, i.e., to a system of free particles and neglects the possibility of their mutual inter-actions. If we want to apply it to actual systems, i.e., a real gas or a solid, we have to postulate forces between the molecules which is outside the framework of the method and whose inclusion will require some kind of application of the kinetic theory. Secondly it is applicable to a system whose energy is constant, i.e., an isolated system. In practice the assumption of perfect heat isolation is also an ideal condition hard to fulfill, and more often we have to deal with systems which are in thermodynamic equilibrium at a definite temperature T. This particular circumstance, however, creates no great difficulty since it can be shown that even for a thermodynamic system maintained at the temperature T, say by immersion in a heat-bath, the energy is more or less constant, the fluctuations of energy being very small. The mathematical technique employed in the method has also been criticised by Fowler, particularly the use of Stirling's theorem, in evaluating the factorials even when at least some of the occupation numbers are not large. Again the most probable distribution was taken to represent the actual distribution, the distributions deviating from this 'maximum set' of occupation numbers being disregarded; rigorously speaking, we ought to take the average or mean distribution.

All these difficulties have been surmounted in the elegant method given by Gibbs. He constructs a purely fictitious *ensemble* or assembly of a huge number of identical systems, each system being an exact 'mental' copy of the actual system under consideration, having same structure and the same energy but distributed over all possible dynamical states or phases of the system (called complexions) through which the actual system will pass in course of time by virtue of its motion according to dynamical laws. We contemplate here all these dynamical or microscopic states at the same instant of time. To picture this ensemble we imagine a phase space of Nr dimensions where N denotes the number of molecules in the actual system of interest and r the number of co-ordinates necessary for specification of the molecule. For a monatomic gas of N molecules the space will be of $6N$ eimensions, $3N$ co-ordinates being necessary to specify the position and $3N$ for the momenta of the molecules. This space is called *system phase space* or γ-space and any dynamical state of the system will be represented by a point in this $6N$-dimensional phase space. These points are called *phase points* and their number per unit volume of the phase space the *phase density* of these points.

The motion of these phase points in the phase space can be investigated from dynamical laws of motion since the points refer to an actual dynamical system which is subject to dynamical laws. For this purpose the phase space is constructed in generalised co-ordinates and generalised momenta. Applying the equation of continuity to the 'flow' of these phase points Liouville showed[1] that

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,\,p} = -\sum_{i=1}^{i=3N}\left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right), \quad . \quad . \quad (42)$$

where ρ is the density of the phase points at the points q, p at time t. Thus if $\rho = f(E)$ where E is the energy of the system and is constant with time for a conservative system, the right-hand side of (42) becomes

$$-\frac{\partial \rho}{\partial E}\sum\left(\frac{\partial E}{\partial q_i}\dot{q}_i + \frac{\partial E}{\partial p_i}\dot{p}_i\right) = 0,$$

since the expression under the Σ must vanish for a conservative system. Thus if $\rho = f(E)$, $\left(\frac{\partial \rho}{\partial t}\right)_{q,\,p} = 0$, i.e., the ensemble is *stationary*. Further it can be shown that ρ is invariant to a canonical transformation. Now since the distribution in the ensemble does not alter with time, it follows that the value of any property, averaged over the systems in the ensemble, will be independent of time.

Now we make the fundamental postulate of statistical mechanics which runs as follows :—*There is equal a priori probability for the phase points to lie in the different regions of the phase space provided the different regions have extensions of same magnitude and correspond to the same energy.* (Attempt is sometimes made to obtain a justification for this postulate from the *ergodic hypothesis* which assumes that the system actually goes through all the dynamical states compatible with the energy of the system, but this is open to criticism). From this postulate it follows that the *time average of any quantity for the system will be simply equal to the ensemble average.* Thus the determination of any average property for the system resolves itself, from the statistical point of view, into a simple determination of the average over the ensemble. This brings out the importance of the Gibbsian ensemble and its relationship to the actual system.

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[1] For proof see Lindsay, *Introduction to Physical Statistics* (1941), Chap. VI, §5 or Tolman, *The Principles of Statistical Mechanics* (1938) Chapter III, §19.

We have seen above that for a stationary ensemble, $\rho = f(E)$. Gibbs assumed that $\rho = N\, exp\left(\frac{\psi - E}{\theta}\right)$ where N is the total number of systems in the ensemble. This is called the *canonical ensemble*. It assumes a wide range of energy values and is eminently suited for the representation of a system at a fixed temperature. Some other investigators assumed $\rho =$ constant, in the small energy interval E and $E + \triangle E$ and zero outside this interval. This is called the *microcanonical ensemble* and is well adapted to the representation of a system with a fixed energy. (The treatment given in §9·4 et seq. in effect deals with such a case). Since all these ensembles satisfy the condition $\rho = f(E)$, they will be in statistical equilibrium i.e. independent of time.

The Maxwell-Boltzmann distribution law can be easily deduced by constructing a canonical ensemble for a system of n free particles. From the distribution $\rho = N\, exp\, (\overline{\psi - E/\theta})$ over the ensemble, it is evident that the probability that the system has the energy E and lies in the phase region

$$\prod_{j=1}^{n} dx_j\, dy_j\, dz_j \prod_{j=1}^{n} dp_{xj}\, dp_{yj}\, dp_{zj}$$

i.e., equal to

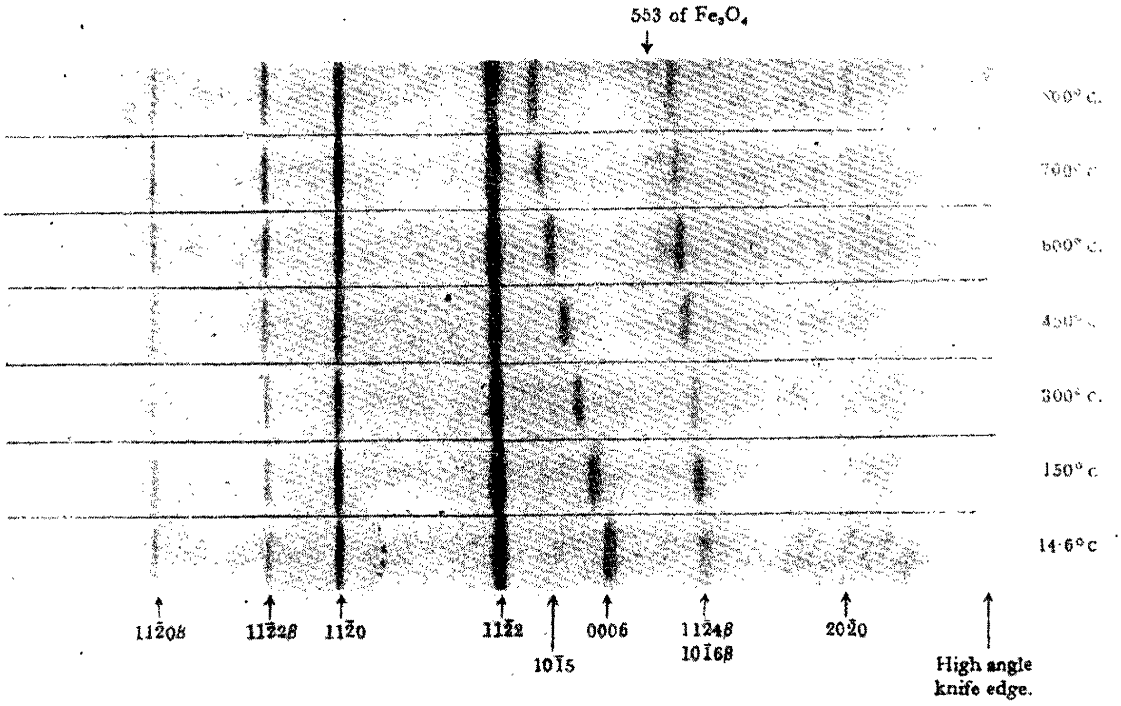
$$\frac{e^{-E(p)/\theta} \prod_{j=1}^{n} dx_j\, dy_j\, dz_j\, dp_{xj}\, dp_{yj}\, dp_{zj}}{\int \ldots 6n \ldots \int e^{-E(p)/\theta} \prod_{j=1}^{n} dx_j\, dy_j\, dz_j\, dp_{xj}\, dp_{yj}\, dp_{zj}}$$

The probability for the momenta p_1, (or momenta components p_{x1}, p_{y1}, p_{z1}) for one molecule can be obtained by integrating the above expression for all values of the variables for the other molecules, and readily yields Maxwell's velocity distribution law. For details see Lindsay, *loc. cit.* Chap. VI, §10.

9·13. Darwin and Fowler's Method.—In this method, as in Maxwell-Boltzmann method, the actual system is considered and the distribution of the N molecules of the system (say gas) in each of the possible energy intervals is investigated, the molecules being regarded as indistinguishable. Instead of the most probable value, however, the *average value* is calculated by making use of the method of contour integration and the use of Stirling's theorem is avoided. It is feared, however, that this mathematical method is beyond the capacity of ordinary students of physics. This method is given in Note 16 at the end of the book (see Appendix).

PLATE I

Fig. 12.—X-ray powder photographs of graphite at various temperatures. The photographs were taken with unfiltered manganese radiation (α - doublet, β).



Books Recommended

1. R. B. Lindsay, *Introduction to Physical Statistics* (1941), John Wiley & Sons.
2. E. Schrödinger, *Statistical Thermodynamics* (1946), Cambridge University Press.
3. J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (1940), John Wiley & Sons.
4. L. Landau and E. Lifshitz, *Statistical Physics* (1938), Oxford University Press.
5. R. C. Tolman, *The Principles of Statistical Mechanics* (1938), Oxford University Press.
6. Fowler and Guggenheim, *Statistical Thermodynamics* (1939), Cambridge University Press.
7. R. H. Fowler, *Statistical Mechanics* (1936), Cambridge University Press.
8. L. Brillouin, *Quanten-statistik*.
9. M. Dole, *Introduction to Statistical Thermodynamics* (1954), Prentice-Hall, Inc. New York.
10. D. ter Haar, *Elements of Statistical Mechanics* (1954), Rinehart & Co., Inc. New York.
11. G. S. Rushbrooke, *Introduction to Statistical Mechanics* (1949), Clarendon Press, Oxford.
12. R. W. Gurney, *Introduction to Statistical Mechanics* (1949), Mc Graw-Hill Book Co.
13. W. C. Band, *An Introduction to Quantum Statistics* (1955), D. Van Nostrand Co.

CHAPTER X

EQUATION OF STATE FOR IMPERFECT GASES

10·1. Deviation from the Perfect Gas Equation.—By the term 'Equation of State' is meant the mathematical formula which expresses the relation between pressure, volume and temperature of a substance in any state of aggregation. If any two of these quantities be known, the third has a fixed value depending uniquely upon them, and can be determined if the equation of state is known, but this is seldom possible. According to the laws of Boyle and Charles we have for a perfect gas the equation of state

$$pV = RT. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

But even Boyle himself found that the law held only under ideal conditions, *viz.*, at high temperature and at low pressure. For every temperature a curve can be drawn which has for its abscissa the volume and for its ordinate the corresponding pressure of the enclosed substance. These curves are called *isothermals*. If equation (1) were true the isothermals ought to be rectangular hyperbolas parallel to each other, but experiments show that this is very seldom the case. The most extended earlier investigations are due to Regnault. He applied pressures up to 30 atmospheres while the temperature was varied from 0° to 100°C. He plotted the product pV as ordinate against p as abscissa (see Figs. 6, 7 supra this chapter). From equation (1) these curves ought to be straight lines parallel to the x-axis, since pV should remain constant; actually however they were found to be inclined to it. Regnault found that for air, nitrogen and carbon dioxide the product pV decreases with increasing pressure, while for hydrogen it increases. Thus these permanent gases were shown to be imperfect.

Later work by Natterer[1], Andrews and Cailletet using higher pressures confirmed the idea that all gases showed considerable deviations from equation (1). Andrews' experiments are of fundamental importance as they throw much light on the actual behaviour of gases and form the basis of an important equation of state first proposed by van der Waals. Andrews' experiments are described in the next section.

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[1] *Phil. Trans.*, **159**, 575, 1869; **166**, 421, 1876.

The most thoroughgoing and exact experiments are due to Amagat[1] who investigated the behaviour of various gases up to a pressure of 3,000 atmospheres. His results, particularly with CO_2 (Fig. 7) and ethylene, showed that their behaviour is very complicated.

An entirely different method was adopted by K. Onnes[2], who investigated the behaviour of several gases at very low temperatures and found that none of the numerous equations of state proposed (section 10·11) correctly represents the results of experiments. As mentioned in §1·7, he found that at any temperature the result is best represented by an empirical equation of the type[3]

$$pV = A + Bp + Cp^2 + Dp^3 + \dots \qquad (2)$$

where A, B, C,..... are constants for a fixed temperature, but vary with temperature in a complicated manner. As many as twenty-five constants were used; they are called *virial coefficients*. A is called the first virial coefficient, B the second virial coefficient, C the third virial coefficient and so on. A is simply equal to RT since for $p \to 0$, eqn. (2) should reduce to that for a perfect gas, *i.e.*, eqn. (1). Holborn and Otto[4] studied several gases up to 100 atmospheres and between the temperatures of $-183°$C. and $+400°$C., and found that they need take only four constants. At ordinary temperatures B is found to be negative

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[1] *Ann. Chim. Phys.*, **28**, 456, 464, 1883; **29**, 68, 1893.

[2] *Leiden Commun.*, No. **71**, 1901.

[3] Sometimes the equation is put in the form

$$pV = A + \frac{B_v}{V} + \frac{C_v}{V^2} + \dots \qquad (2a)$$

In this equation, as in (2), $A = RT$ since the perfect gas law should hold at zero density. Substituting the value of p from this equation in the terms on the right of equation (2) and equating the coefficient of $1/V$ and $1/V^2$ with those in (2*a*) we get $B_v = BRT$; $C_v = A(B^2 + CA)$. Sometimes an expansion for pV/A in power series of $1/V$ is employed and pV/A is called the *virial*.

[4] *Zeits. f. Physik*, **33**, 9, 1925.

for oxygen, nitrogen and air, and positive for hydrogen and helium, etc. C is always positive.

The coefficient B is of particular importance. For all gases it is found to vary in a similar way: at low temperatures it has a negative value, then as the temperature is raised it gradually increases to zero and becomes positive. The temperature at which $B = 0$ is called the *Boyle Temperature*[1] T_B, for at this temperature Boyle's law will hold upto fairly high pressures provided C, D are negligible, as can be seen from the relation

$$\frac{\partial}{\partial p}(pV) = B + 2\,Cp + 3\,Dp^2 \cong 0. \quad . \quad . \quad . \quad . \quad (3)$$

Boyle's law will however be more accurately obeyed at that pressure which accurately satisfies the equality in (3) with the terms in C, D retained. Thus for every pressure there will be a corresponding Boyle temperature and the Boyle temperature used in the literature corresponds to zero pressure.

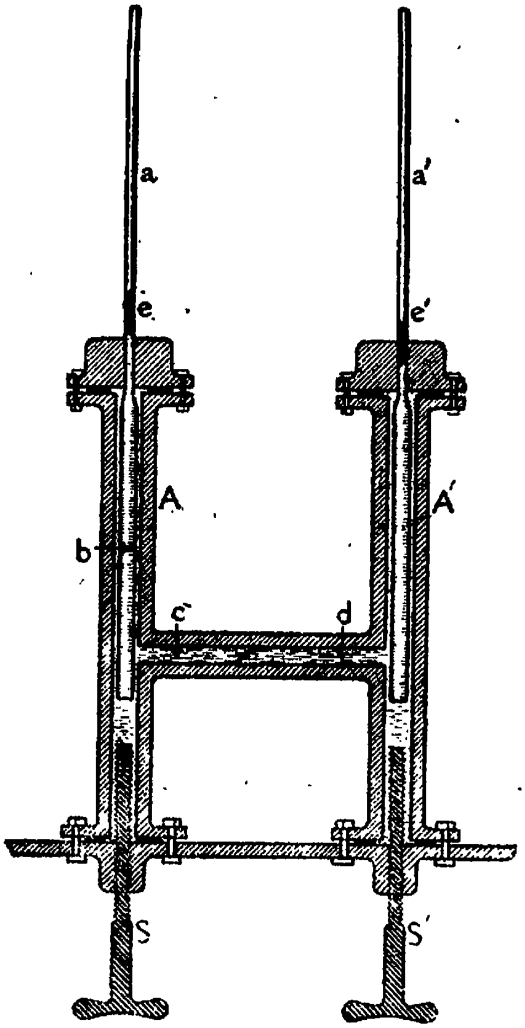

Fig. 1.—Andrews' apparatus.

10·2. Andrews' Experiments.—While engaged in the attempt to liquefy some of the so-called permanent gases Andrews, in 1869, was led to study the isothermals of carbon dioxide. His apparatus is indicated in Fig. 1.

ab is a glass tube whose upper portion consists of capillary tube and is narrower than the lower part. Carefully dried carbon dioxide was passed through the tube for several hours and then the tube sealed at both ends. The lower end of the tube was immersed under mercury and opened, and some of the gas expelled by heat, so that, on cooling, a small column of mercury *e* rose in the tube and enclosed the experimental gas.

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[1] This is sometimes called the Boyle point.

The tube was surrounded by a strong copper tube A fitted with brass flanges at either end, to which brass pieces could be attached air-tight with the help of rubber washers. A screw S passed through the lower flange. The tube A contained water and hence by screwing in, pressures as high as 400 atmospheres could be applied to the carbon-dioxide enclosed above *e*. To register the pressure a similar capillary tube containing air was placed on the right side, and was enclosed in a tube A′ exactly similar to A, with which it communicated through the tube and thus the pressures in both the tubes were always kept equal. The pressures in either tube could be varied by means of the screws S or S′. The capillary tube *ae* could be surrounded by any suitable constant temperature bath (not shown).

10·3. Discussion of Results.—The curves obtained by Andrews are shown in Fig. 2. Let us consider the isothermal corresponding to 13·1°C. Starting from the right we see (portion AB) that as we increase the pressure, the volume diminishes considerably and finally liquefaction of the gas begins at a pressure of about 49 atmospheres (point B). As long as liquefaction continues the pressure remains constant and the volume continually diminishes, more and more of the gas being precipitated as liquid. This is indicated by the horizontal line BC. At C all the gas has condensed into liquid and the almost vertical rise of the curve indicated by CD corresponds to the fact that liquids are only slightly compressible.

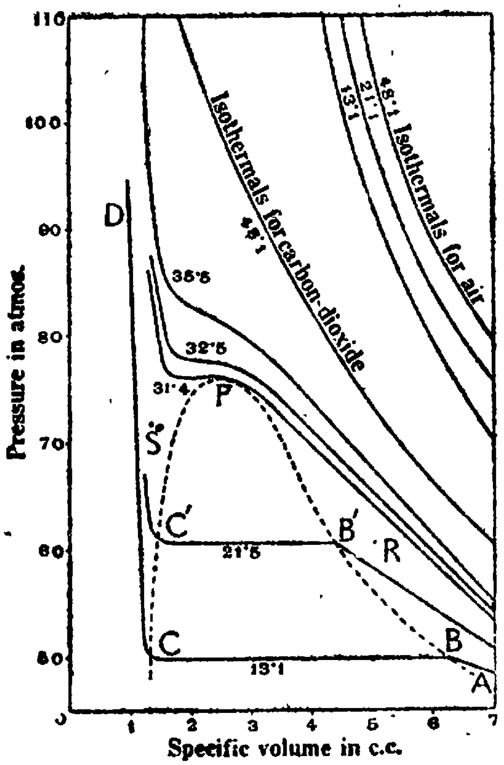

Fig. 2. Isothermals for Carbon-dioxide obtained by Andrews.

The isothermal corresponding to 21·5°C. is of the same general form but the horizontal portion B′C′ is shorter. In this case the specific volume of the vapour, when condensation begins, is smaller while that of the liquid, when condensation has completed, is greater than the corresponding quantities for the isothermal at 13·1°C. As the temperature is raised these changes proceed in the same direction as above, till at 31·4°C, the horizontal part has just disappeared and the two volumes have become identical. This is called the *critical isothermal* for carbon-dioxide. Above this temperature the horizontal part is absent from all the isothermals and as we increase the pressure, there is no visible formation of liquid, but the volume diminishes rapidly till it becomes equal to that of the liquid at that temperature. This peculiarity of the isothermal also disappears at higher temperatures as is evident from the isothermal for 48·1°C, which is much like the isothermals for air shown separately on the right-hand top.

We thus see that the whole diagram for carbon dioxide is divided by the critical isothermal into two essentially different regions. Above this isothermal no liquid state is at all possible even under the greatest pressure, while below it there are three separate regions. In the region enclosed by the dotted curve whose highest point P, called the critical point, lies on the critical isothermal, both liquid and gaseous states co-exist. To the left of the line PC and below the critical isothermal there is the liquid region while to the right of PB there is the gaseous region. Now if, by means of gradual changes we want to convert gaseous CO_2 at 25°C. and 60 atmos. pressure (represented by the point R) into liquid CO_2 at the same temperature (represented by the point S) without any discontinuity appearing, *i.e.*, the mass is not to separate into a liquid and a gaseous part with a layer between them, we must avoid reaching the inside of the dotted curve BB′PC′C. Thus we heat the substance above 31·4°, then compress it till the volume becomes equal to that of the liquid at that temperature. Next cool it to 25°C. and then reduce the pressure. Thus starting from the point R which undoubtedly represents a gaseous state we are able to reach the point which undoubtedly represents a liquid state, while at no stage of the operation any heterogeneity or meniscus appears in the whole mass. This result is expressed by the statement that there exists *a continuity of the liquid and gaseous states* and was established by the experiments of Andrews.

Thus we see that if gaseous carbon dioxide is compressed above 31·4°C. no liquid can make its appearance, however great the pressure may be. More accurate experiments show that this temperature is 31·0 and not 31·4°. The temperature 31·0°C. is called the *critical temperature* (T_c) for carbon-dioxide. We may define critical temperature[1] as the highest temperature at which a gas can be liquefied by pressure alone. This is why the earlier attempts to liquefy permanent gases failed, though enormous pressures amounting to as much as 3,000 atmospheres were sometimes employed. The pressure just necessary to liquefy the gas at the critical temperature is called the *critical pressure* (p_c) and the volume which the gas[2] then occupies, *i.e.*, at the critical temperature and critical pressure, is called the *critical volume* (V_c). These three quantities are called the *critical constants* of the gas. A table containing the critical constants for various gases is given in §10·17. It obviously follows that in trying to liquefy a gas, it is useless to apply pressure alone if the initial temperature is above the critical point, and no pressure greater than the critical need be employed.

10·4. Van der Waals' Equation of State.—The equation of state for perfect gases was deduced theoretically from the kinetic theory of gases in §3·12. Two important assumptions were made in the deduction of this equation :

(1) the molecules were considered to be negligibly small in size;

(2) the gas was supposed to have only kinetic energy and no potential energy.

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[1] Critical temperature may also be defined as the temperature at which all the properties of the liquid and the vapour become identical.

[2] Of course the volumes occupied by the gas and the liquid at the critical temperature are the same.

It is now known that both these assumptions are only approximate and very nearly hold in case of extremely rarefied gases, only, *i.e.*, when the pressure is very small. Clausius was the first to point out that the molecules, though extremely small in size, cannot be regarded as geometrical points, and account must be taken of their size in the calculation of pressure.

It is evident that the space available for the free motion of the molecule becomes less when molecular size is taken into account because one molecule cannot lie within the space occupied by other molecules. Due to this reduction in available space, the number of molecular collisions per second is increased producing an increase of pressure on any surface over the previously calculated value. Evidently the decrease b in the volume V of the gas must be related to the total volume occupied by the molecules and V in the perfect gas equation has to be replaced by $V-b$.

Hirn, in 1864, pointed out that the molecules must exert forces of attraction on one another since a solid or liquid can be held together only by such intermolecular attractions. Hence the energy of a gas cannot be wholly kinetic, and potential energy due to forces of cohesion should also be taken into account. But the credit of first working out a systematic theory, taking into account both these factors, goes to van der Waals. He first clearly discussed the matter in 1873 in his classical essay *On the Continuity of Liquid and Gaseous States*, and put forward the equation

$$\left(p+\frac{a}{V^2}\right)(V-b)=RT. \quad . \quad . \quad . \quad (4)$$

This equation is found to hold approximately for small deviations from the perfect gas equation and gives a general idea of the course of isothermals for gases but is no better than a mere first approximation, even at low densities. It is however widely used for its simplicity. A comparison of this with the experimental results is given in §10·7.

10·5. Deduction of van der Waals' Equation.—Van der Waals made the simplifying assumption that the molecules are hard spheres of diameter σ and attract each other with a weak force which depends only upon the inter-molecular distance and not upon the orientation of the molecules, the force practically vanishing at distances several times σ. We shall also suppose that the molecular density is small so that the effects of molecular size and of molecular attraction are small and we interest ourselves in seeking a first-order correction to the perfect gas equation. Van der Waals made the calculation in two steps. First he considered the effect of the finite size of the molecules treating them as hard spheres without external fields. Next he calculated the effect of the weak attractive field and superposed it on the former volume effect. The procedure cannot be rigorously justified, but we shall follow it in this section.

Suppose the volume contains N molecules, where N is the Avogadro number. In finding the possible positions for any particular molecule, we regard this molecule as a point at its centre and imagine the other $N-1$ molecules as spheres of radius σ, and consider the assembly of this point and the $N-1$ spheres of influence. The space available for the point molecule is

$$V-(N-1)\frac{4\pi\sigma^3}{3} = V-\frac{N.4\pi\sigma^3}{3}(\text{nearly}) = V-2b,$$

where $b = 4(4/3)\pi N(\sigma/2)^3$ = four times the volume of the gas molecules in a gram-molecule of the gas[1]. Hence the probability of finding the centre of a molecule in the element of volume dV which is such that it is not contained within the sphere of influence of any molecule is

$$\frac{NdV}{V-2b}. \qquad (5)$$

since all regions are equally probable as no forces are supposed to exist between the molecules.

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[1] But the centre of the molecule cannot lie within a distance $\frac{1}{2}\sigma$ from the boundary; thus the effective volume is further diminished by the volume of a layer of thickness $\frac{1}{2}\sigma$ parallel to the boundary but this volume is generally negligible compared with the volume of the vessel. Further we are disregarding the possibility of two spheres of influence intersecting each other, which is approximately justified at low molecular densities.

Now we have to find out the probability that the element dV does not lie in the $N-1$ spheres of influence. It is important to note that half of every such sphere, which is away from the boundary, is *a priori* excluded for the element dV. This is not quite obvious and presents some difficulties inherent in the static picture of the gas we have assumed. It is however easily understood if we consider the collisions with the wall which are a very essential feature of the mechanism for the generation of pressure though the method of probabilities does not require them, but obviously van der Waals' equation cannot hold if this did not occur.

In the collision of the sphere of influence with the wall, it is obvious that the element dV cannot lie in that half of the sphere of influence which is away from the boundary because if it were to lie there, the molecule, whose centre is contained therein, could not collide with the wall; this is however not the case since all molecules do collide with the wall. Thus the more distant hemisphere is automatically and *a priori* excluded and the element dV can only lie in that hemisphere which is nearer the boundary. This will be so for all the spheres of influence. Thus the total effective volume of the spheres of influence in which dV can at all lie is only $(N-1)\frac{2}{3}\pi\sigma^3 = \frac{2}{3}N\pi\sigma^3 = b$. Hence the probability that the element dV lies in these spheres of influence is b/V and the probability that it does not lie there is $1-b/V$.

Hence the probability[1] that the centre of a molecule lies in the element dV where dV is selected at random is given by the product of this probability and that expressed by (5), that is by

$$\frac{N\,dV}{V-2b} \times \left(1 - \frac{b}{V}\right) = \frac{NdV}{V-b} \text{ approx.} \quad . \quad . \quad (6)$$

Had we neglected the dimensions of the molecule the probability would have been NdV/V. Hence the net result of taking into account the size of the molecules is that the effective volume is not V but $V-b$. Thus the ordinary gas equation $pV = RT$ should be modified into

$$p(V-b) = RT. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

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[1] It will be noticed that we have considered only binary encounters and neglected ternary and higher encounters.

This method of proof was first given by van der Waals and is open to objection at certain points. The same equation can however be deduced as a first approximation under the above-mentioned assumptions by a variety of methods, *viz.*, from the virial theorem of Clausius (§10·9), from statistical mechanics (§10·13), from a consideration of collisions[1] with the boundary or any imaginary surface in the interior of the gas, etc.

The correction for the weak attractive or cohesive forces can be very simply obtained. The molecules attract one another with a force which varies inversely as some power of the distance between them. Thus the force will be appreciable only at small distances and is negligible at large distances. Now a molecule in the interior is acted on by forces in all directions and hence on the average these will balance. But this is not so with a molecule in the surface or close to the surface. The components of the forces acting on it resolved parallel to the surface will balance but not those in a perpendicular direction. There will be a resultant force acting perpendicular to the boundary and directed *inwards*. It is obvious that this force on a single molecule will be proportional to the number of attracting molecules in the fluid, *i.e.* to the number n of molecules per c.c. The force acting per unit area of the surface will be proportional to the product of the above force and the number of molecules in that area of the surface. Hence this cohesive pressure p_1 acting per unit area of the surface is proportional to n^2. Now $n = N/V$ where N is the total number of molecules and V the total volume. Therefore $p_1 \propto 1/V^2 = a/V^2$ where a is a constant, proportional to the square of the total number of molecules in the gas, *i.e.*, proportional to the square of the mass of gas taken. This *cohesive pressure* is sometimes called *internal pressure* or intrinsic pressure and acts only in the boundary layer in any solid or fluid giving rise to the phenomenon of surface tension in liquids and tensile forces in solids. It opposes, the *kinetic*[2] *pressure*, but assists the external pressure in keeping the substance together. Thus it opposes the outward motion of the molecules and decreases their momentum and hence also the pressure generated by their impact. Clearly therefore the pressure developed will be less than that calculated previously by this *cohesive pressure*, i.e., a/V^2. In other words, we must replace p in the perfect gas equation by $p+a/V^2$ as if the external pressure p on the gas is increased by a/V^2.

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[1] See Kennard, *Kinetic Theory of Gases*, §122, or Fowler, *Statistical Mechanics* (1936), §9·8.

[2] The kinetic pressure is that given by the relation $p_k = RT/V$.

Hence equation (7) must be further modified into[1]

$$\left(p+\frac{a}{V^2}\right)(V-b)=RT. \quad . \quad . \quad . \quad . \quad (4)$$

This is van der Waals' equation of state for an imperfect gas. Various other equations of state have been proposed of which a few important ones will be discussed later. Some of them explain the experimental results better than van der Waals' equation. We shall consider only the latter in great detail as it is very simple.

We may remark that the b-correction really arises from the force acting between molecules when they are just the distance σ apart (i.e., during collision) which is a repulsive force. Thus the a and b terms should arise from a single intermolecular force which is an attractive force when the intermolecular distance is large but becomes a repulsive force when the distance equals σ. For further discussion see §10·9.

10·6. Methods of finding the Values of '*a*' and '*b*'.—The chief methods of finding the values of '*a*' and '*b*' occurring in van der Waals' equation are given below :--

(1) *From the pressure and volume coefficients of expansion.*

The *pressure coefficient* of expansion β may be defined by the relation $\beta=\frac{1}{p}\frac{dp}{dT}=\frac{1}{p}\cdot\frac{\Delta p}{\Delta T}$. If the gas obeys van der Waals' law

$$p=\frac{RT}{V-b}-\frac{a}{V^2},$$

we have
$$\frac{dp}{dT}=\frac{R}{V-b}=\left(p+\frac{a}{V^2}\right)\frac{1}{T} \text{ from (4).}$$

Or
$$T\frac{dp}{dT}-p=\frac{a}{V^2}. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Therefore
$$\frac{a}{V^2}=Tp\left(\beta-\frac{1}{T}\right). \quad . \quad . \quad . \quad . \quad . \quad (9)$$

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[1] If we consider n mols of the substance, the constant '*a*' must be multiplied by n^2 and '*b*' by n.

Equation (9) directly gives the magnitude of the cohesive force at any temperature and shows that it is proportional to the pressure p and hence to the density of the gas. Further the equation shows that the pressure coefficient of expansion β depends upon the volume V and hence upon the density of the gas.

If we represent by β the mean pressure coefficient between 0 and 100°C, we get

$$\frac{a}{V^2} = T_0 p_0 \left(\beta - \frac{1}{T_0}\right), \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where the suffix 0 refers to the corresponding quantities at 0°C. For a perfect gas $\beta = 1/T_0$ and hence $a/V^2 = 0$.

The mean *volume coefficient* α is defined as

$$\alpha = \frac{V_1 - V_0}{T_1 - T_0} \frac{1}{V_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where the suffix 1 refers to 100°C. Applying van der Waals' equation for the two temperatures T_0, T_1 we have

$$\left(p + \frac{a}{V_0^2}\right)(V_0 - b) = RT_0, \quad . \quad . \quad . \quad (12)$$

and

$$\left(p + \frac{a}{V_1^2}\right)(V_1 - b) = RT_1. \quad . \quad . \quad . \quad (13)$$

Subtracting (12) from (13) and neglecting the product ab which is a small quantity of the second order, we get

$$p(V_1 - V_0) + a\left(\frac{1}{V_1} - \frac{1}{V_0}\right) = R(T_1 - T_0). \quad . \quad . \quad (14)$$

Dividing (12) by (14), we have

$$\frac{T_0}{T_1 - T_0} = \frac{(p + a/V_0^2)(V_0 - b)}{p(V_1 - V_0) + a\left(\frac{1}{V_1} - \frac{1}{V_0}\right)}.$$

Hence

$$\alpha = \frac{V_1 - V_0}{T_1 - T_0} \cdot \frac{1}{V_0} = \frac{1}{T_0} \frac{(p + a/V_0^2)(V_0 - b)}{pV_0 - a/V_1}$$

$$= \frac{1}{T_0}\left[1 + \frac{a}{pV_0}\left(\frac{1}{V_0} + \frac{1}{V_1}\right) - \frac{b}{V_0}\right], \quad . \quad . \quad . \quad (15)$$

neglecting small quantities of second and higher orders;

or

$$\alpha - \frac{1}{T_0} = \frac{1}{T_0}\left[\frac{a}{pV_0}\left(\frac{1}{V_0} + \frac{1}{V_1}\right) - \frac{b}{V_0}\right]. \quad . \quad . \quad (16)^1$$

---

[1] If 'a', 'b' are supposed to be known, say by methods (2), (3), (4), equations (10) and (16) may be employed to determine T_0, the temperature of melting ice as given by a perfect gas thermometer. It is easily seen that $\beta > 1/T_0 > \alpha$. Thus T_0 can be obtained sufficiently accurately. For further discussion see Loeb, *Kinetic Theory of Gases*, pp. 162-165 (1934).

Equation (16) may be employed to find 'b' when 'a' and the volume coefficient α have been already determined. α is seen to depend upon the volume and the pressure in a complicated way.

We shall illustrate this method by means of an example. For air Chappuis gives $\beta = 0\cdot0036744$ at a pressure of 1000 mm. of mercury. Therefore from (10)

$$\frac{a}{V^2} = (\beta T_0 - 1)p_0 = (0\cdot0036744 \times 273\cdot2 - 1)\,\frac{1000}{760} = 0\cdot00501 \text{ atm./cm.}^2$$

Consider a mass that occupies 1 c.c. at atmospheric pressure; the volume at a pressure of 1000 mm. is 0·76. Hence $a = 0\cdot00289$ atmos. $\times \text{cm}^4$.

Similarly the value of 'b' may be calculated from (16) but as it occurs there as a difference of two large terms, its value cannot be determined accurately by this method.

(2) *Constant Volume method.*—A very simple and accurate method of determining 'a' and 'b' is the following :—

We confine ourselves to a narrow region and determine 'a' and 'b' point by point. Thus from van der Waals' equation

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{V-b} \therefore b = V - R\Big/\left(\frac{\partial p}{\partial T}\right)_v \quad . \quad . \quad . \quad (17)$$

And from (8)

$$a = V^2\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] . \quad . \quad . \quad . \quad (18)$$

Thus 'a' and 'b' can be obtained by observing the rate of increase of pressure with temperature as in a constant volume gas thermometer. When determined in this way they are found to vary with temperature. In table[1] 1 the values of 'a' and 'b' for argon at various temperatures are given. The values refer to a gram-molecule of the gas N.T.P. 'a' is here expressed in atmospheres$\times$cm.^{4} and 'b' in c.c.

Table 1.—*Variation of* 'a' *and* 'b'

T°K	$a\times10^{-6}$	b	T	$a\times10^{-6}$	b
151·2	1·90	61	193·2	1·69	51
157·2	1·87	59·5	213·2	1·60	48
163·2	1·84	58	233·2	1·53	45
173·2	1·785	55·5	253·2	1·47	43
183·2	1·735	53	273·2	1·42	41

(3) *Isothermal method.*—The values of 'a' and 'b' may also be obtained by a study of the isothermals of a gas. Thus we have

$$p = \frac{RT}{V-b} - \frac{a}{V^2}\,; \quad \left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}.$$

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[1] Taken from Onnes and Crommelin, *Leiden Commun.*, No. 131 (c).

From these two simultaneous equations 'a' and 'b' can be evaluated if $(\partial p/\partial V)_T$ is found from the study of isothermals.

(4) *Determination of 'a' and 'b' from critical data.*—In the next section it will be shown from theoretical considerations that the critical temperature T_c, critical pressure p_c and critical volume V_c for a gas obeying van der Waals' equation are respectively given by

$$T_c = \frac{8a}{27b\mathrm{R}};\ p_c = \frac{a}{27b^2};\ V_c = 3b. \qquad . \quad . \quad (19)$$

$$\therefore a = \frac{27\mathrm{R}^2}{64}\cdot\frac{T_c^2}{p_c};\ b = \frac{\mathrm{R}}{8}\cdot\frac{T_c}{p_c} \qquad . \quad . \quad . \quad (20)$$

Thus if T_c, p_c are experimentally determined 'a' and 'b' can be calculated with the help of equation (20). It may however be pointed out that this method is not at all reliable as the van der Waals' equation is not expected to hold in the critical region where the density is high, van der Waals' equation being only valid as a first approximation at low densities.

(5) *Determination of 'a' and 'b' from the Joule-Thomson effect*[1].—In Chapter XII it is shown that the temperature of inversion T_i for the Joule-Thomson effect is given by $T_i = 2a/b\mathrm{R}$. Knowing 'a' by the foregoing methods, say (1), the value of 'b' may be calculated from the temperature of inversion.

The values of 'a' and 'b' for a few important gases are given in Table 2. They refer to 1 c.c. of gas[2] at N. T. P., and are determined by method (4) from equations (20). In view of what is said in method (4) no great reliance may be put on these values.

Table 2.[3]—*Values of 'a' and 'b' for some gases.*

Substance	$a\times10^6$ in atmos.$\times$cm.^{4}	$b\times10^6$ in c.c.
Helium ..	6·8	106
Argon ..	268	143
Oxygen ..	273	143
Nitrogen ..	272	173
Hydrogen ..	48·7	118
Carbon-dioxide ..	717	191
Ammonia ..	833	168

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[1] This will be understood after Chapter XII has been read.

[2] If we consider a gram-molecule we have to multiply 'a' in the table by $(22{\cdot}4\times10^3)^2$ and 'b' by $22{\cdot}4\times10^3$. This is obvious from relation (20) since R for a gram-molecule in these units (atmos.$\times$cm.^{3}) is $22{\cdot}4\times10^3/273$.

[3] Taken from Landolt and Börnstein, *Physikalisch-chemische Tabellen.*

Problems.—1. Using the values of $T_c = 5{\cdot}3$, $p_c = 2{\cdot}25$ atmos., calculate 'a' and 'b' for a gram-molecule of helium gas.

2. Calculate the critical temperature and critical pressure of helium from the following values of the constants :—$a = 6{\cdot}15 \times 10^{-6}$, $b = 9{\cdot}95 \times 10^{-4}$ per gram-molecule, where the unit of pressure is the atmosphere, and the unit of volume the volume of the gas at N. T. P.

10·7. Discussion of van der Waals' Equation.— We shall now discuss in detail the van der Waals' equation (4). This is an equation of the third degree in V, hence it follows that for every value of p, V should have three values. Further, from the theory of equations, either all the three values are real or one is real and two imaginary.

Again writing the equation in the form

$$p = \frac{RT}{V-b} - \frac{a}{V^2}, \quad . \quad . \quad . \quad . \quad (21)$$

we see that for very large values of V, p is small and in the limit $p = 0$ when $V = \infty$. Again when V is very small approaching b, p tends to infinity. Hence the curve must have a concavity upwards. Further V cannot be less than b for then p would be negative which is physically absurd.

If in (21) we substitute the values of 'a' and 'b' for carbon dioxide,, *viz.*, $a = 0{\cdot}00717$ atmos., $b = 0{\cdot}00191$ c.c. and then represent the resulting equation by means of graphs for every temperature (p = ordinate, V = abscissa), curves of the type shown in Fig. 3 are obtained. It is readily seen that the curves resemble, in general, the

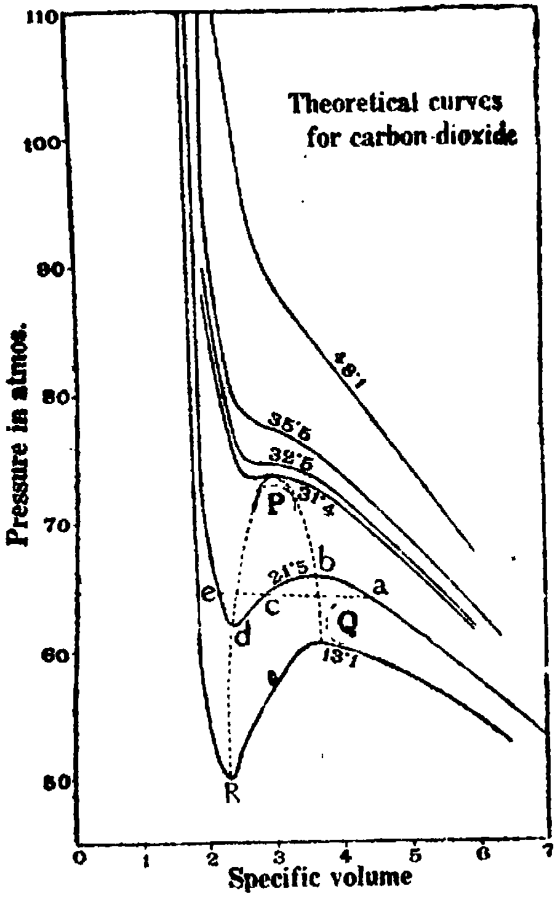

Fig. 3. Theoretical curves for CO_2 according to van der Waals' equation.

experimental curves (Fig. 2) obtained by Andrews, but if we look for quantitative agreement by trying to make the two sets of curves exactly overlap we are greatly disappointed. In fact the agreement is only approximate and qualitative, partly because of errors in the assumed values of '*a*' and '*b*' and partly because the equation holds only approximately.

There is however a remarkable divergence between the theoretical and the experimental curves in one region. The theoretical curves drawn from van der Waals' equation give maxima and minima in the region represented by a straight line in Andrews' curves. Experimentally this is the region where condensation or vaporisation begins and the pressure remains constant as long as the process continues.

This difference is easily explained when the theoretical curve is properly interpreted. The part *bcd* inside the dotted curve indicates that the volume should decrease with decrease of pressure. This would be a collapsible state, for any decrease of volume is accompanied by a decrease of pressure which tends to decrease the volume further. (This is apparent if we imagine the fluid to be confined in a cylinder). Thus the state *bcd* of the fluid inside the dotted curve represents a state of equilibrium which is highly unstable towards small differences of pressure or density and consequently can never be realised in practice with all the substance in one phase only. This is why the part *bcd* is not obtained in Andrews' experiments. The portion *ab* obviously represents *supersaturated vapour or undercooled vapour* since this corresponds to the liquid state in stable equilibrium at a higher temperature as is evident by a reference to Andrews' experimental curves. Now under certain conditions an undercooled vapour is sometimes obtained but as is well known the equilibrium can be easily disturbed by mechanical shocks, introduction of particles of dust, etc. Hence the portion *ab* which represents undercooled vapour in metastable equilibrium does not occur in Andrews' curves which represent only states of stable equilibrium. Similarly the portion *de* represents a superheated liquid which is also in metastable equilibrium, and hence does not occur in Andrews' curves. Thus the apparent divergence is explained.

In the foregoing we have explained the discrepancy between the theoretical and experimental curves on the basis of the factual instability of equilibrium. The reason why the equilibrium becomes unstable can be seen from considerations of thermodynamics by calculating the Gibbs function (Chap. VIII) for a van der Waals gas. It can be shown[1] that of the three volumes corresponding to *a*, *c*, *e*, which the substance can have at a certain pressure, the one of lower volume is stable if the pressure is higher than a certain value, and the larger volume is stable if the pressure is lower than that value, the intermediate volume *c* being always unstable. Thus if stable states alone are to occur the transition will take place along the straight line *ace*. The second law of thermodynamics can be used in a very simple way to tell us when condensation begins, *i.e.*, where the straight part commences. A simple thermodynamic argument[2] shows that the straight line should be so drawn that the area *abc* = area *cde*. When the straight line is so drawn, *a* and *e* are both stable states.

The maxima and minima points on the theoretical curve can be obtained by putting $(\partial p/\partial V)_T = 0$. Hence from (21), by differentiation,

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0 \; ; \qquad (22)$$

or

$$T = \frac{2a(V-b)^2}{RV^3}. \qquad (23)$$

This is also a cubic equation. Hence for every isothermal there are three real or one real and two imaginary points of maxima or minima. The curves below P in Fig. 3 are seen to possess one maxima and one minima points while those above it have none at all. A slight mathematical transformation will show that the other point of minima lies in the region $V < b$ and hence has no physical meaning. Equations (21) and (23) when combined yield

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[1] For details see Slater, *Introduction to Chemical Physics* (1939), p. 188, published by McGraw-Hill Book Co. or Keenan, *Thermodynamics*, Chaps. XXIV & XXV.

[2] Let the substance represented by the point *a* form the working substance of a heat engine (Chap. IV) and let it be taken through the cyclic operation represented by the path *abcdeca*. Since the temperature remains constant throughout the process, it follows from the theory of heat engines (Chap. IV) that the total work done by the working substance, *i.e.*, the area of the enclosed curve is zero. Hence the two areas *abca* and *cdec*, since they are described in opposite senses, must be equal.

$$p = \frac{a(V-2b)}{V^3}. \quad . \quad . \quad . \quad . \quad . \quad (24)$$

This is the curve passing through the maxima and minima points and is shown by the dotted curve QPR.

In Fig 2 all isothermals lower than P cut the dotted curve BB'PCC' at two points, and therefore liquefaction can be observed by changing the pressure along them. For the critical isothermal, *i.e.*, the isothermal corresponding to the critical temperature, these two points have coalesced into one. Referring to Fig. 3, it is readily seen that the isothermal passing through the point P where P is a point of inflexion for the family of curves or a maxima point for the dotted curve, is the critical isothermal because below P every isothermal has got maxima and minima points while above P there are none at all. As we have seen above if the isothermal has got maxima and minima points there must be a liquefaction of the gas and we can find out the position where liquefaction begins. For liquefaction there must be two points on the curve having equal pressure. The highest isothermal for which this condition is satisfied is the one passing through the point P since at P the maxima and minima have coalesced into one. Hence P must be identified with the critical point and the isothermal through it with the critical isothermal. Now for P to be the maximum point of the dotted curve we have, by differentiating (24) with respect to V and equating to zero,

$$\frac{a}{V^3} - \frac{3a(V-2b)}{V} = 0; \quad \text{or } V_c = 3b.$$

Hence from (24) and (21) we have

$$p_c = \frac{a}{27b^2}, \quad T_c = \frac{8a}{27Rb}, \quad \frac{RT_c}{p_c V_c} = \frac{8}{3}. \quad . \quad . \quad (25)$$

The critical constants may be very easily deduced from (21) since for the critical isothermal the point P is a maximum point as well as a point of inflexion, and at this point both $(\partial p/\partial V)_T$ and $(\partial^2 p/\partial V^2)_T$ are equal to zero.

Hence from (21)

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0. \qquad (22)$$

$$\frac{\partial^2 p}{\partial V^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0. \qquad (26)$$

Combining (22) and (26) we get $V_c = 3\,b$, and with the help of (22), $T_c = 8a/27bR$. Finally from (21) $p_c = a/27b^2$, and $RT_c/p_cV_c = 8/3$.

10·8. Defects in van der Waals' Equation.—In spite of the fact that van der Waals' equation enables us to describe the general features of transition from liquid to gaseous state, there is considerable discrepancy if we attempt a quantitative test of this equation. We have already shown that for carbon-dioxide the curves drawn from van der Waals' equation do not exactly coincide with the experimental curves of Andrews. A particular isothermal may be made to agree much more closely with suitably chosen values of '*a*' and '*b*', but then for the same values of *a* and *b* the agreement is not so good for other isothermals. This only implies that '*a*' and '*b*' vary with temperature as has been directly found from experiments (see p. 408 table 1), but van der Waals' theory assumes them to be constant. This is a great shortcoming of the theory.

Table 3.—Critical Coefficients for various fluids.

Substance	Critical coefficient	Substance	Critical coefficient
Helium	3·27	Chlorobenzol	3·78
Hydrogen	3·276	Iodobenzol	3·78
Neon	3·249	Bromobenzol	3·80
Nitrogen	3·412	Ethyl ether	3·81
Argon	3·424	Hexane	3·83
Oxygen	3·419	Heptane	3·86
Carbon-dioxide	3·45	Octane	3·86
Ethane	3·55		
Methyl chloride	3·48	Propyl alcohol	4·00
Sulphur dioxide	3·62	Ethyl alcohol	4·02
Carbon-tetrachloride	3·67	Methyl alcohol	4·55
Isopentane	3·73	Acetic acid	4·99
Benzol	3·75		
Pentane	3·76		

Again van der Waals' equation gives $V_c = 3b$, while experimentally it is found that V_c is more nearly equal to $2b$.

A more definite discrepancy however lies in the values of the critical coefficient RT_c/p_cV_c. From equation (19) this should be 8/3 for all gases independent of their nature. Actually, however, it varies from gas to gas with an average value of 3·7 for most substances. This constant appears to depend upon the molecular structure of the gas. The critical coefficients for various gases are given in Table[1] 3.

It should be pointed out, however, that it is not proper to test van der Waals' equation by investigating its behaviour in the critical region as on account of the very assumptions in its theoretical deduction, it is not expected to hold at such high densities. That the discrepancy at such high densities is not even greater shows that van der Waals' assumptions are not very wide of the truth. A better, though less spectacular, agreement should be expected when we compare the behaviour at low densities. This will be done in §10·12.

10·9. Deduction of Equation of State from the Virial Theorem of Clausius.[2]—Clausius[3], proceeding in an entirely different manner, deduced the equation of an imperfect gas more rigorously. We can treat the gaseous particles as ordinary matter subject to classical dynamics. Thus if x, y, z denote the coordinates of the centre of any molecule measured with respect to a certain system of axes, and X, Y, Z denote the components of the force acting on the molecule, we must have

$$m\frac{d^2x}{dt^2} = X;\quad m\frac{d^2y}{dt^2} = Y;\quad m\frac{d^2z}{dt^2} = Z. \qquad (27)$$

Proceeding as in §3·45 we can easily deduce

$$\frac{1}{2}m\dot{x}^2 = \frac{m}{4}\frac{d^2}{dt^2}(x^2) - \frac{1}{2}Xx. \qquad (28)$$

Similarly for the other coordinates. Adding these we have

$$\frac{1}{2}m(\dot{x}^2+\dot{y}^2+\dot{z}^2) = \frac{m}{4}\frac{d^2}{dt^2}(x^2+y^2+z^2) - \frac{1}{2}(Xx+Yy+Zz),$$

which gives the kinetic energy of a molecule.

Let us sum this expression over all molecules of the gas and take average over a sufficiently long time τ. We get

$$\frac{1}{2}\overline{\sum mc^2} = \frac{m}{4}\overline{\sum\frac{d^2}{dt^2}(r^2)} - \frac{1}{2}\overline{\sum(Xx+Yy+Zz)}, \qquad (29)$$

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[1] Taken from *Handbuch der Physik*, **10**, p. 143.

[2] An excellent treatment of the virial theorem is given in Clemens-Schaefer, *Einführung in die Theoretische Physik*, Vol. 2. See also *Handbuch der Physik*, **10**, pp. 127—130.

[3] *Phil. Mag.*, 1870. *Ann. d. Physik*, **2**, pp. 124, 141 (1870).

where the summation Σ extends over all molecules and the bars denote time average from 0 to τ. If the gas is in a steady state the quantities $\frac{1}{2}\Sigma mc^2$ and $\Sigma\,(Xx+Yy+Zz)$ are approximately constant throughout the motion. The second term in equation (29) is equal to

$$\frac{m}{4}\,\frac{1}{\tau}\int_0^{\tau}\sum \frac{d^2}{dt^2}(r^2)\;dt = \frac{m}{4}\sum\frac{1}{\tau}\left[\frac{d}{dt}(r^2)\right]_0^{\tau}.$$

Now $\frac{d}{dt}(r^2) = 2r.\frac{dr}{dt}$, and $\frac{dr}{dt}$ for a molecule fluctuates irregularly with time, being as often positive as negative, while 'r' from the theory of Brownian movement varies as the square root of time. Hence by making τ large, the term $\frac{1}{\tau}\left[\frac{d}{dt}(r^2)\right]_0^{\tau}$ becomes effectively zero[1] and (29) reduces to[2]

$$\frac{1}{2}\overline{\Sigma\, mc^2} = -\frac{1}{2}\Sigma\,\overline{(Xx+Yy+Zz)}. \quad . \quad . \quad (30)$$

The expression on the right was called by Clausius the *virial* of the system. Equation (30) asserts that *the total kinetic energy of translation of the molecules of a gas in the steady state is equal to its virial. This is the virial theorem of Clausius.*

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[1] We might look at the problem in a slightly different way. $\Sigma\, mr^2 = I$ the moment of inertia of the gas about the origin and this must remain constant on the average if the gas is enclosed by actual walls. Therefore, $\frac{d}{dt}\,\Sigma\, mr^2$ will have some value which cannot display any steady increase or decrease with time.

[2] The same result is obtained even when we take frictional forces opposing molecular motion into account (See R. H. Fowler, *Statistical Mechanics*, 1936, §9·7) provided we assume that the frictional forces are small enough to permit of an effectively steady state. In fact, the essential difference between the present treatment and that given on p. 187 is that in the Brownian movement the frictional forces are too great to permit the attainment of a steady state of equilibrium distribution. In other words in the Brownian movement phenomena there are no normal stresses across any physical or imaginary geometrical boundary and hence in that case X, Y, Z do not include any boundary forces and consequently their contribution ultimately vanishes when averaged over a large number of particles. In the present case of molecular motion the frictional forces are small and a steady state is attained. The frictional term will give $\overline{\sum\frac{1}{4}\frac{d}{dt}(cr^2)} = \frac{1}{4\tau}\left[c\,\Sigma\, r^2\right]_0^{\tau}$ on the right hand side of (29) and since $m\,\Sigma\, r^2$ is nearly constant, the value of the frictional term will be zero if we take average over a long time.

Now X, Y, Z include all the forces which ever act upon the molecules and we must find the contribution of all such forces to the virial. These forces may be broadly divided into the following three categories :—

(1) The force of impact on the molecule due to collision with the walls of the containing vessel.

(2) The forces due to collision between two molecules.

(3) The forces of attraction between molecules when separated by some distance.

Let us calculate the contribution of (1) to the virial. Imagine the gas confined in a parallelepiped with sides a, b, c, parallel to the coordinate axes while the two bc faces cut the x-axis at x_1, x_2 ($\therefore x_2-x_1=a$). If the pressure exerted by the gas is p, the value of ΣX at x_1 is $p.bc$, that at x_2 is $-p.bc$.

$$\therefore -\tfrac{1}{2}\Sigma Xx = \tfrac{1}{2}pbc(x_2-x_1) = \tfrac{1}{2}p.\, abc = \tfrac{1}{2}pV,$$

where V is the volume of the parallelepiped. Similarly for the other pairs of faces. Hence the total contribution by the forces acting at the walls is $\tfrac{3}{2}pV$. Further if we assume the gas to be perfect, the forces mentioned in (3) do not exist, and since the size of the molecules is negligible for a perfect gas the contribution due to forces in (2) is nil as action and reaction are equal and of opposite sign and in this case they also act at the same place. Hence for a perfect gas we have from the theorem of virial

$$\frac{1}{2}\, mN\overline{c^2} = \frac{3}{2}pV,\ pV = \frac{1}{3}\, mNC^2 \quad . \quad . \quad .(31)$$

in agreement with equation (9) of Chap. III.

For a real gas however we must take into account the effect of the forces acting between the molecules of the gas including the forces during collision, assuming at the same time that the molecules have finite size. The nature of these forces is not definitely known. For the present let us assume that the force between two molecules is radial and is equal to $\phi(r)$ where r is the distance between the molecules. It is thus assumed to depend only upon the inter-molecular distance and not upon the orientation of the molecules. $\phi(r)$ will be considered positive when it is repulsive. Evidently $\phi(r) = -dE/dr$ where E is the potential energy due to the intermolecular force. Let the coordinates of the centres of the two molecules be x, y, z and x',

y', z' respectively. Then the components X, Y, Z and X', Y', Z' of the forces acting on them will be given by

$$X = \phi(r)\frac{x-x'}{r}\ ;\ X' = \phi(r)\frac{x'-x}{r}.$$

The contribution to ΣXx made by these forces is

$$Xx+X'x' = \frac{\phi(r)}{r}(x-x')^2. \quad . \quad . \quad . \quad (32)$$

Similarly for the other components. Hence the total contribution by the inter-molecular forces to the virial is

$$-\frac{1}{2}\sum\frac{\phi(r)}{r}\left\{(x-x')^2+(y-y')^2+(z-z')^2\right\} = -\tfrac{1}{2}\Sigma r\phi(r),$$

where the summation extends over each pair of molecules counted once. Hence the virial theorem yields

$$\tfrac{1}{2}mN\overline{c^2} = \tfrac{3}{2}pV-\tfrac{1}{2}\Sigma r\phi(r). \quad . \quad . \quad . \quad . \quad (33)$$

But we have already shown in Chap. III that the mean kinetic energy of translation $\tfrac{1}{2}m\overline{c^2}=\tfrac{3}{2}kT$. Hence (33) yields

$$pV = NkT+\tfrac{1}{3}\Sigma r\phi(r). \quad . \quad . \quad . \quad . \quad (34)$$

This is the general form of the equation of state derived from the virial theorem and holds accurately. Thus if we could calculate the value of the term $\Sigma r\phi(r)$ accurately we could obtain an exact equation of state. Unfortunately this is not possible since $\phi(r)$ is not known precisely. We shall therefore attempt to calculate an approximate value of $\Sigma r\phi(r)$.

In order to proceed further we have to use the distribution law. According to Maxwell-Boltzmann law

$$n_c = n_0(m/2\pi kT)^{3/2}\, e^{-(\frac{1}{2}mc^2+E)/kT}\, .4\pi c^2.\, dc,$$

where n_c denotes the number of molecules per c.c. having velocity lying between c and $c+dc$ and having the potential energy E. n_0 is the molecular density in regions where the potential energy is zero. Integrating for all values of c from 0 to ∞ we get[1]

$$n_r = n_0\, e^{-E/kT} \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Let us calculate the contribution of one molecule to the virial. The average number of other molecules lying within a distance r to $r+dr$ from this molecule is $n_r.4\pi r^2.dr$ and for these the force is $\phi(r)$. Hence the contribution of one molecule to $r\phi(r)$ is

$$4\pi r^3.\ n_0 e^{-E_r/kT}.\ \phi(r).dr,$$

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[1] It might be argued that (35) does not hold when E is negative for then we cannot integrate for c from 0 but from some minimum value c_0. Actually however (35) holds even for negative mutual potential energies and can be rigorously deduced from statistical mechanics.

and the contribution of N molecules of the gas is

$$\frac{N}{2}\int_0^\infty 4\pi r^3 n_0 e^{-E_r/kT}\phi(r).dr, \quad . \quad . \quad . \quad . \quad (36)$$

the division by 2 being necessary since every pair has to be counted only once. We have written E_r for E meaning thereby that the potential energy is due to the particular molecule considered at the distance r and is not due to forces exerted by other molecules. This is justified only when the intermolecular force is a short-range force and in addition the molecular density is small so that the molecule is effectively within the field of force of a single molecule and ternary and higher interactions are negligible. Thus equation (36) is only a first approximation and cannot rigorously apply to liquids. The limit of integration has been made infinity instead of the boundary of the container as the integrand varies so rapidly that the difference between the two is negligible.

Further n_0 is not[1] equal to N/V since on account of the intermolecular force varying with distance the distribution of molecular density will not be uniform. Since however this is a correction term and we interest ourselves only in a first-order correction we can substitute the approximate value of $n_0=N/V$ in this correction term. Equation (34) then yields

$$pV=NkT+\frac{2\pi}{3}\frac{N^2}{V}\int_0^\infty r^3.\,e^{-E_r/kT}\phi(r)\,dr. \quad . \quad . \quad (37)$$

This equation can be written in a slightly modified form. Since $\phi(r)=-\partial E_r/\partial r$, we have

$$\int e^{-E_r/kT}\phi(r)dr = kT.e^{-E_r/kT}+A,$$

where A is the constant of integration. Integrating (37) by parts and utilising the result we obtain

$$\begin{aligned} pV &= NkT+\frac{2\pi}{3}\frac{N^2}{V}\cdot\left[\left\{r^3\left(kT\,e^{-E_r/kT}+A\right)\right\}_0^\infty \right.\\ &\qquad \left. -\int_0^\infty 3r^2\left(kTe^{-E_r/kT}+A\right)dr\right] \\ &= NkT+\frac{2\pi N^2}{V}kT.\int_0^\infty r^2\left(1-e^{-E_r/kT}\right)dr, \quad . \quad . \quad (38) \end{aligned}$$

where A has been put equal to $-kT$ to secure the convergence of the integral at infinity, since E_r being small at infinity the term {} gives r^3E_r which vanishes at infinity as E_r is negligible. Eqn. (38) is correct as a first-order approximation for spherically symmetrical type of molecular field.

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[1] With the assumption of rigid molecules without external force-field it can be shown that $n_0=\frac{N}{V}\left(1-\frac{b}{V}\right)$.

Investigations have shown that the force $\phi(r)$ between two molecules at large distances is an attractive force increasing rapidly as the distance decreases, and finally when the repulsion begins to be stronger the net attractive force decreases till ultimately the force becomes a very strong repulsive one when the molecules come very close together. It is however not possible to evaluate the integral in (38) accurately without actually knowing E_r.

As mentioned in §10·5 van der Waals made the simplifying assumption that the molecules are rigid spheres of diameter σ and attract each other with a weak force which rapidly decreases as the distance increases. Thus we may regard the molecules as kept apart by a repulsive force of enormous intensity at distance σ with E_r increasing from 0 to ∞ in an infinitesimal range at the value $r=\sigma$, *i.e.*, $E_r=\infty$ for $r<\sigma$. On account of the attractive force E_r has a small negative value for $r>\sigma$. With these assumptions the integral in (38) becomes

$$\int_0^\sigma r^2\,dr+\int_\sigma^\infty r^2\left(1-e^{-E_r/kT}\right)dr=\frac{\sigma^3}{3}+\int_\sigma^\infty r^2\frac{E_r}{kT}\,.\,dr \text{ approx.}$$

Equation (38) then yields

$$pV=RT+\frac{RT}{V}\left(b-\frac{a}{RT}\right), \quad . \quad . \quad . \quad . \qquad (39)$$

where

$$b=\frac{2}{3}N\pi\sigma^3,\ a=-2\pi N^2\int_\sigma^\infty r^2E_r\,dr. \quad . \quad . \qquad (40)$$

b is the same as van der Waals' constant and a is positive since E_r is negative. Thus the second virial coefficient $B_v=bRT-a$, and inspite of the approximations made, this value is exact under the assumptions of van der Waals as a more accurate calculation[1] involving ternary and higher encounters affects only terms in higher powers of $1/V$.

For the sake of comparison van der Waals' equation should be expanded in powers of $1/V$. Thus

$$p=\frac{RT}{V-b}-\frac{a}{V^2}=\frac{RT}{V}\left(1-\frac{b}{V}\right)^{-1}-\frac{a}{V^2},$$

or

$$pV=RT+\frac{RT}{V}\left(b-\frac{a}{RT}\right)+RT\left(\frac{b}{V}\right)^2+\ldots\ldots, \quad . \qquad (41)$$

which agrees with (39) as for as the second virial coefficient. The third virial coefficient occurring in (41) is not correct as can be shown from more elaborate theoretical calculations. Thus van der Waals' equation (4) is theoretically correct only upto terms in $1/V$ and no further (though it contains a term in $1/V^2$ also) even for a gas obeying van der Waals' assumptions. It is more accurate to use equation (39) though (4) is generally used on account of its simplicity but its success is limited. The fact that equation (39) is found to hold fairly well shows that van der Waals' assumptions contain a good deal of truth.

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[1] See Boltzmann, *Vorlesungen über Gastheorie*, **2**, §51, or Ursell, *Proc. Camb. Phil. Soc.*, **23**, 685, 1927.

10·10. Variation of '*a*' and '*b*'.—Accurate experiments[1] show that '*a*' and '*b*' of van der Waals' equation are not quite constant but vary with temperature and volume at which they are measured (see table 1). We shall now try to explain why it is so.

The variation of '*a*' is due to the action of the attractive forces in changing the concentration of the molecules. Evidently this change in molecular concentration will be less effective the higher the kinetic energy or the temperature of the gas. Thus '*a*' is a function of T and decreases as T rises. This is verified from Table 1, p. 408. An expression for the internal pressure p_i due to attractive forces has been deduced from rigorous mathematical considerations by R. H. Fowler[2] and is given in eqn. (38). From this

$$a = 2\pi n^2 kT \int_0^\infty r^2 (e^{-E/kT} - 1)\, dr, \quad . \quad . \quad . \quad . \quad (12)$$

which shows clearly that '*a*' is a function of T. The exact explicit dependence cannot be obtained unless the nature and magnitude of the attractive forces between molecules are accurately known.

The variation of b with temperature can be more easily accounted for. From our present knowledge of molecular structure, it is clear that the molecules cannot have an invariable diameter σ as assumed by van der Waals, but will have some softness with a slightly extended force-field. Obviously the smallest distance of approach between the centres of two molecules will vary with the energy of impact of the molecules, *i.e.*, the temperature of the gas. If at ordinary temperatures this distance is r_0, then at higher temperatures the impacts will be more violent and the molecules will approach each other to a distance less than r_0. It is thus clear that the effective diameter of the molecule will be a slowly varying function of the temperature. Further we saw that the van der Waals' equation is correct only if $(b/V)^2$ is neglected. Hence it is obvious that the equation will be correct for values of V much greater than b and not for values of V comparable with b. It follows that b will not remain constant but will be a function of V. We therefore conclude that b will be a function of the temperature as well as of volume, and probably similar is the case with a. This is why the values of a and b for one isotherm do not fit those for another isotherm.

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[1] See Jellinek, *Lehrbuch der physikalischen Chemie*, Vol. I, part I, p. 391; Jabloczinski, *Phys. Zeits.*, **33**, 536, 1932.

[2] R. H. Fowler, *Statistical Mechanics* (1929), p. 214.

10·11. Other Equations of State.[1]—The defects of van der Waals' equation of state have been pointed out in §10·8. It is mentioned there that according to experiments

$$V_c = 2b\,;\quad RT_c/p_cV_c = 3\cdot 70.$$

Any other equation of state must satisfy these conditions and its accuracy must be judged by the degree to which it approximates to these results.

There are two methods by which later workers have attempted to improve van der Waals' equation. The first consists in adding empirical constants which can be suitably chosen, and the second consists in obtaining a more accurate expression from rigorous theoretical considerations. We shall first consider the former.

The well-known equation of this type is that of Clausius[2], *viz.*,

$$\left\{ p + \frac{a'}{T(V+c)^2} \right\} (V-b) = RT. \quad . \quad . \quad . \quad (43)$$

Comparing it with van der Waals' equation we see that here 'a' has been modified into a'/T. This has some theoretical basis also since 'a' must vary with temperature. Instead of V we have $V+c$ where c is another constant. This equation fits Andrews' curves better than van der Waals' equation, but fails in case of other gases, and hence has no advantage over van der Waals' equation.

Another empirical equation was proposed by D. Berthelot, *viz.*,

$$\left(p + \frac{a'}{V^2T}\right)(V-b) = RT, \quad . \quad . \quad . \quad (44)$$

or in the modified[3] form

$$pV = RT\left\{ 1 + \frac{9\,p_r}{128\,T_r}\left(1 - 6T_r^{\,2}\right)\right\} \quad . \quad . \quad . \quad (45)$$

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[1] No less than 56 equations of state have been proposed. For a list of these see Partington and Shilling, *Specific Heat of Gases*, pp. 29-33, or *Handbuch der Experimental-physik*, Vol. VIII, Part 2, p. 224.

[2] *Wiedem. Ann.*, **9**, 337, 1880. In the general form he puts $f(T)$ in place of a'/T.

[3] Equation (44) may be treated as on p. 413 to yield the value of the critical constants in terms of a' and b. Substituting these values of a' and b in (44) and altering the resulting equation so as to agree with certain experimental results and making approximations, equation (45) is obtained. For details of this deduction see Partington and Shilling, *Specific Heat of Gases.*

where $p_r = p/p_c$ and is called the reduced pressure and $T_r = T/T_c$ and is called the reduced temperature (§10·15). The equation in the latter form contains only observed critical constants and is often employed for practical purposes. It gives better agreement than van der Waals' equation over a wider range as it approximates better to the theoretical expression (38).

Dieterici[1] from semi-theoretical considerations, deduced the equation

$$p = \frac{RT}{V-b} e^{-\frac{a}{RTV}} \quad . \quad . \quad . \quad . \quad . \quad (46)$$

Generally speaking this equation is more correct than van der Waals'; this is due to the exponential instead of the additive form of the correction for adhesive forces. It yields $V_c = 2b$ and $RT_c/p_cV_c = 3{\cdot}695$, the agreement being thus better than in the case of van der Waals' equation. If a and b are small, (46) reduces to the van der Waals' equation.

Saha and Bose[2] deduced from thermodynamic considerations and the theory of probability (Chap. IX) the equation

$$p = -\frac{RT}{2b} e^{-\frac{a}{RTV}} \log_e \left(\frac{V-2b}{V}\right), \quad . \quad . \quad . \quad (47)$$

which also yields van der Waals' equation as a special case. In this equation the critical coefficient $RT_c/p_cV_c = 3{\cdot}53$, which gives a better agreement with the experimentally obtained values for simpler gases.

Beattie and Bridgman[3] have suggested an equation of state of the form

$$p = \frac{RT}{V^2}\left(1 - \frac{c}{VT^3}\right)\left(V + B_0 - \frac{bB_0}{V}\right) - \frac{A_0}{V^2}\left(1 - \frac{a}{V}\right) \quad . \quad (48)$$

containing five adjustable constants. They find that by suitably choosing the values of the five constants, this equation fits the data for at least fourteen gases (including all the commoner ones) to within 0·5 per cent down to the critical point over a wide range of pressure. Its chief value however is its utility as it has no satisfactory theoretical basis.

A review of the values of the critical coefficient (p. 414) shows that it cannot have a fixed value for all substances, but the value should depend partly on the actual structure of the molecule and the state of association. It is therefore perhaps futile to attempt to deduce any single equation of state which should be valid for all substances in general. Recently attempts have been made to deduce equations which may be valid for individual gases.

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[1] *Wiedem. Ann.*, **66**, 826, 1898; **69**, 685, 1899; *Drud. Ann.* **5**, 51, 1901. Jeans has tried to place it on a rigorous theoretical basis (see Jeans, *Dynamical Theory of Gases* (1921), p. 161.

[2] *Phil. Mag.*, **36**, 199, 1918.

[3] *Jour. Amer. Chem. Soc.*, **49**, 1665, 1927; *Zeits. f. Phys.*, **62**, 95, 1930.

Reinganum[1] deduced quite rigorously from the virial theorem the equation[2]

$$\left(p + \frac{a(T)}{V^2}\right)\left(V - be^{-c/RT}\right) = RT,$$

where $a(T)$ implies that a is a function of the temperature. The exact values of $a(T)$ and c can be found only when the intermolecular forces are accurately known.

Fowler[3] has deduced equation (38) from the virial theorem as a first approximation considering only binary encounters[4]. The problem of determining the potential energy E or the intermolecular force $\phi(r)$ still remains.

On account of the difficulty in obtaining the equation of state in a closed form Kamerlingh Onnes proposed the equation of state in the form of a series expansion (equation 2*a*). This procedure is now widely adopted and attempts are made to evaluate the virial coefficients from theoretical considerations and compare them with the observed values.

10·12. Second Virial Coefficient.—The second virial coefficient B_v is found experimentally by fitting the observational data on gases in equation (2) or (2*a*) retaining three or four terms on the right-hand side. As stated on p. 397 it is found to depend on the temperature. Van der Waals' equation is often tested at ordinary pressures by plotting B_v against T as abscissa. According to van der Waals' equation (41), $B_v = bRT - a$ and thus the plot should be a straight line whose slope will give b and the intercept will give a. The experimental curves for various gases (Fig. 4) are almost rectilinear but have some convexity[1] showing that van der Waals' equation is only approximately true even at low densities. We have seen in §10·9 that for a gas obeying van der Waals' assumption of rigid spherical molecules with weak and symmetrical attracting fields the relation $B_v = bRT - a$ should hold rigorously (see eqn. 39). The present discrepancy is therefore evidently due to the fact that van der Waals' assumptions are not accurately (but only approximately)

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[1] *Phys. Zeits.*, **2**, 241, 1901; *Ann. d. Physik*, **10**, 334, 1903.

[2] For the deduction of this equation see Loeb, *The Kinetic Theory of Gases* (1934), pp. 156-160.

[3] *loc. cit.* p. 211.

[4] Ursell (*Camb. Phil. Soc. Proc.*, **23**, 685, 1927) has employed the method of statistical mechanics to calculate the higher virial coefficients by considering ternary and higher encounters.

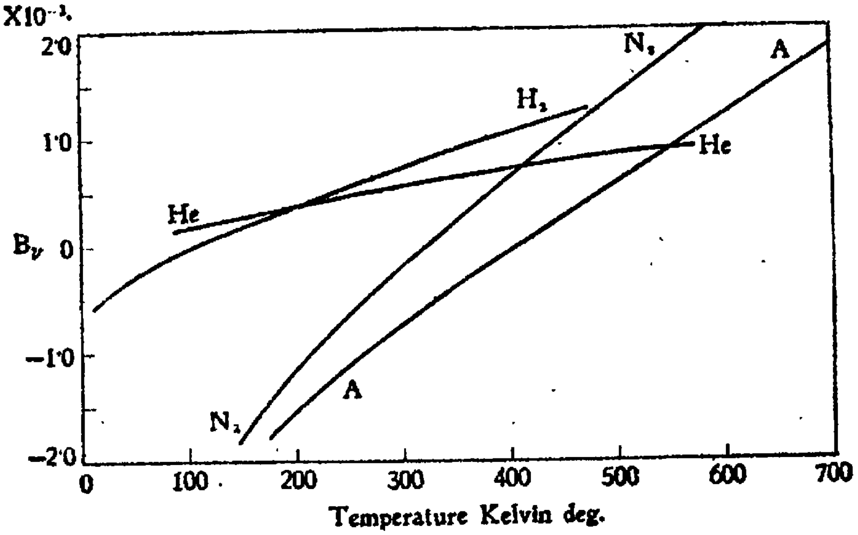

Fig. 4.—Variation of B_v with temperature.

obeyed by the actual gases as already pointed out in §10·10. The problem of theoretically determining B_v therefore requires a correct knowledge of the intermolecular force $\phi(r)$ or the intermolecular potential energy E_r since

$$B_v = 2\pi RT.\, N \int_0^\infty r^2 \left(1 - e^{-E_r/kT}\right) dr, \quad . \quad . \quad (49)$$

from (38). Subsequent attempts are mainly concerned with the determination of such a law of force as will agree with the observed values of B_v. For a comprehensive account of the work done on the subject see Kihara, *Rev. Mod. Phys.*, Vol. 25, p. 831 (1953).

10·13. Derivation of Equation of State from Statistical Mechanics.—The equation of state for a perfect gas can be readily obtained by utilising the statistical expression for entropy S (Eqn. 37,

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[1] By drawing tangents to the curve at different points and assuming eqn. (41) to apply, the apparent values of a and b at different temperatures can be found.

p. 390). Using this expression we obtain for the free energy F (p. 343) the result $F = -RT.\ ln\ f$, and the partition function

$$f = \Sigma e^{-\epsilon_r/kT} = \frac{V}{g}\ (2\pi mkT)^{3/2}$$

As shown on p. 391 it is necessary to divide this value of $Nk\ ln\ f$ by $k\ ln\ N!$ to take into account the identity of the molecules. Hence f should be multiplied by e/N. Therefore

$$F = -RT\ ln\frac{V}{g}(2\pi mkT)^{3/2}\ e/N. \quad . \quad . \quad . \quad (50)$$

Since $p = -(\partial F/\partial V)_T$, equation (50) yields $p = RT/V$, the perfect gas equation. In the case of polyatomic molecules there are also present internal energies of rotation and vibration in the molecule but these do not affect the equation of state because f in the above equation has to be simply multiplied by $f_i = \Sigma e^{-\epsilon_i/kT}$ and ϵ_i, the internal energy, does not depend upon the coordinates of position of the molecule and hence upon V.

The derivation of equation of state for an imperfect gas is however complicated as we have to take into account the potential energy of the molecules also. We have to consider the statistics not of independent molecules, but of interacting molecules, and must therefore use the method of Gibbs or of Fowler (§9·12 and 9·13). Making certain approximations the result comes out to be the same as eqn. (38) of p. 419. For details see Slater, *Introduction to Chemical Physics* (1939), Chap. XII §4, or Fowler and Guggenheim, *Statistical Thermodynamics* (1939), Chap. VII. The latter contains full references and various applications also.

10·14. Nature of Molecular Forces.[1]—The equation of state (38) deduced above from theoretical considerations can be of use only when we are able to calculate the force between two molecules. The calculation of this force is a complicated and difficult problem. It is however easy to infer from the observed tendency of matter to aggregate and form liquid and solid states at low temperatures that the molecules must exert forces of attraction on one another. Since the molecules exist as separate entities inspite of this attraction it follows that repulsive forces must come into play at short inter-molecular distances. The simplest model which will give rise to such forces is that of hard impenetrable molecules surrounded by an attractive field as assumed by van der Waals. This picture is however not compatible with the observed compressibility of solids and in particular with the present known structure of atoms and molecules. According to the Rutherford-Bohr model the atom consists of electronic shells round a nuclear positive charge. Hence the force between atoms or molecules is made up of forces between the electrons and the nuclei of the two systems. The force is therefore essentially electrostatic; there are also magnetic forces but they are ordinarily small enough to be neglected.

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[1] For more detailed information see Fowler, *Statistical Mechanics* (C. U. P. 1936), Chap. X, or Slater, *Introduction to Chemical Physics* (1936), Chaps. XXII and XXIV.

Let us consider the force between two neutral atoms or molecules. Exceptf or the atoms having closed shells such as He, Ne, Ar, etc., almost all other atoms are electrically unsymmetrical. Such atoms are electrostatically equivalent to a positive and equal negative charge separated by a distance. This is called an electric dipole or doublet and would possess an electric moment. Molecules composed of such atoms will also behave as dipoles. Many molecules are now known to possess permanent electric moments whose values have been determined from a study of the dielectric properties of gases composed of such molecules. If the dipoles were oriented at random the field at an external point would be zero, but on account of the Boltzmann factor the molecules rotate in such a way that there is a slight preponderance of molecular positions having less potential energy, in which position the dipoles will be parallel to each other, *i.e.*, the positive end of one dipole will be opposite the negative end of the other dipole producing thereby a net attraction between the two dipoles. Thus the effect of dipole-dipole interaction is an intermolecular attraction varying as $1/r^4$, r being the distance between the dipoles.

In most common gases, however, the molecules do not possess dipole moment and the mechanism of interaction is the distortion or polarisation produced by one neutral molecule on another neutral molecule. If the charge distribution is spherically symmetrical as in the case of atoms with closed shell, it follows from ordinary electrostatics, that the force outside the shell will be zero. Even in this case, however, it is unlikely that the electrons will be so arranged in the shells that at every instant during their motions the dipole moment will be zero. (Its time average is of course zero). In fact at any instant the dipole moment will have a small value which will be constantly fluctuating in magnitude and direction on account of the motion of the electrons. The fluctuating dipole moment produces fluctuating external field at a distance r proportional to μ/r^3 where μ is the dipole moment. The fluctuating field produces on the other neutral atom or molecule a displacement of charge or polarization in phase with the field. The force exerted by the fluctuating field on this displaced charge does not average to zero on account of the phase relations but results in a net attraction between the molecules which is van der Waals' attraction. We shall now calculate this attraction and the corresponding van der Waals' energy.

The fluctuating field $F = \mu/r^3$ produced by one molecule distorts the electronic distribution of the other molecule, the electrons moving in the direction opposite to the field. On account of this polarization of the second molecule an induced dipole moment αF, parallel and proportional to the field is produced, α being the *polarizability* of the molecule. On account of the interaction between these two dipoles the second molecule will be attracted towards the first dipole by the force $-\alpha F\frac{\partial F}{\partial r} = \frac{3\alpha\mu^2}{r^7}$. The attractive energy E will be such that $\frac{\partial E}{\partial r}$ will be equal to the above force. Integrating the above expression for force and averaging for all possible orientations of the first dipole, the energy will come out to be $E = -\frac{3}{2}\frac{\alpha\mu^2}{r^6}$. This is van der Waals' attractive energy. If the molecules were originally permanent dipoles, there will be an additional attractive energy term varying as $1/r^3$ as proved previously.

The above attractive forces operate when the atoms are sufficiently far apart. But if the atoms come so close together that they touch or overlap, quite new type of forces, called *Exchange Forces*, come into play. The classical conception of the atom is not able to explain these forces, for the spherically symmetrical shell of charge in one atom will be able to penetrate a sufficient distance inside a similar shell of another atom, without any special repulsion being produced. Thus the atom would appear easily penetrable but this is not so. Actually what happens is that the atoms distort the charge distribution of each other producing either an attraction (*valence binding*) or repulsion (*van der Waals' repulsion*) between the atoms. In many cases, the attractive state is however inaccessible owing to Pauli's Exclusion Principle (See §17·12 and Note 15). (This is always so if we consider such systems in which all possible chemical bonds have already been formed). Thus usually a strong repulsion is produced giving thereby an explanation of the observed impenetrability of the atom. Actually the charges of the atoms are so redistributed in accordance with the exclusion principle that some charge shifts away from between the two nuclei to the outer sides of the nuclei producing a net repulsion between the two atoms. The mutual potential energy of this distorted electronic configuration (called *overlap energy*) can be calculated from wave mechanics and can be shown to approximate to $De^{-\lambda r}$ for large distances r. For short distances the expression is very complicated. We shall therefore assume the empirical formula $E=Ar^{-s}$ for the overlap energy for short distances. 's' is found to lie between 8 and 14. Thus the resultant interaction energy is

$$E = \frac{\lambda}{r^s} - \frac{\mu}{r^t} \quad . \quad . \quad . \quad . \quad . \quad . \quad (51)$$

The intermolecular force will be one power less in r. Substituting the above value of E in the expression (49), B_v can be calculated. Actually however the values of λ, μ, s, t are not definitely known and the process is reversed. Those values of λ, μ, s, t are selected which will fit in with the observed variation of B_v with temperature. The calculations have been made by Born, Fowler, Lennard-Jones and others. The results are, however, not quite unambiguous. t can be set down as 6 and s is found to lie between 8 and 14. For details see Fowler *loc. cit.* pp. 209-306.

By substituting these values of s and t in equations (51) and (38) an accurate equation of state could be determined. Further since s and t are found to vary from gas to gas, it follows that no single equation of state can be strictly valid for all gases. Thus we see that for all practical purposes we have to depend essentially upon empirical equations of the type of Kamerlingh Onnes which are almost always employed in accurate work. The values of the virial coefficients are determined empirically for each individual gas.

10·15. Law of Corresponding States.—We shall now consider an important modification of the equation of state. Taking van der Waals' equation

$$p = \frac{RT}{V-b} - \frac{a}{V^2},$$

and writing $\quad \frac{p}{p_c} = p_r, \; \frac{T}{T_c} = T_r, \; \frac{V}{V_c} = V_r,$

where p_c, T_c, V_c are the critical constants, and again substituting for p_c, T_c, V_c their corresponding values in terms of a and b, *viz.*,

$$V_c = 3b, \; p_c = \frac{a}{27b^2}, \; T_c = \frac{8a}{27Rb},$$

we get $\quad \left(p_r + \frac{3}{V_r^2}\right)\left(V_r - \frac{1}{3}\right) = \frac{8}{3} T_r. \quad . \quad . \quad . \quad (52)$

The quantities p_r, T_r, V_r are respectively called the 'reduced' pressure, 'reduced' temperature and 'reduced' volume of the gas, while (52) is called the 'reduced' equation of state of van der Waals.

Equation (52) does not contain any constant depending upon the nature of the gas. It should therefore be true for all substances and be of universal application. From this, it follows that if *for any two substances any two of the quantities p_r, T_r, V_r possess the same value the third quantity must also be identical.* This is called the *Law of Corresponding States.* Thus if the temperature and pressure of two substances bear the same proportion to their critical temperature and pressure, their volumes will also bear an identical ratio with the respective critical volumes, or, in other words, by suitably expanding or contracting the scales on which p and V are measured, the isothermals of all substances can be made to coincide.

This law is true only approximately and not rigorously. An easy way of showing this is to compare the values of RT_c/p_cV_c for various substances. As already mentioned it varies from 3·0 to 4·9 (see Table 4) while it should remain constant if this law were true. For simpler gases it is very nearly true. Another way of showing the same thing is to draw the isothermals in terms of the reduced pressure and reduced volume for various substances at the same reduced temperature. Then the curves for all substances ought to be coincident, but actually this is not quite so. It may be pointed out that so long as the equation of state contains only two quantities depending upon the nature of the substance, such as van der Waals' 'a' and 'b', it can always be reduced to yield an equation valid for all substances.

De Boer[1] has discussed the law of corresponding states from the point of view of quantum theory. He has shown that this law can be deduced theoretically if we assume that the potential energy can be expressed as a sum of terms all of which depend only on the distance between a pair of molecules and further if classical statistics is assumed to be applicable. There will be deviations from the law due to quantum effects, the extent of deviation depending upon the magnitude of the parameter $h/\epsilon\sigma\sqrt{m}$ where ϵ is a characteristic energy and σ a characteristic length. On this basis various properties of gaseous elements have been examined[2] and fairly close agreement with experimental data has been obtained.

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[1] De Boer and Michels, *Physica*, **5**, 945, 1938; De Boer, *Physica*, **14**, 139, 1948.

[2] De Boer and Blaisse, *Physica*, **14**, 149, 1948; Grilly, Hammel and Sydoriak, *Phys. Rev.*, **75**, 303, 1103, 1949.

10·16. Experimental Study of the Equation of State.—The methods of experimentally determining the isothermals for gases and liquids fall into two classes: (*a*) In the one we observe the change in volume when different pressures are applied. (*b*) In the other volume remains constant, the quantity of matter being varied.

(*a*) *Apparatus based on the principle of variable volume.*—When the pressure is small, the apparatus is quite simple and is given in elementary text-books as the Boyle's law apparatus. For higher pressures up to 100 atmos. an apparatus due to Cailletet may be used. This is described below. The same apparatus with certain modifications has been used by Regnault, Andrews and Amagat in their researches.

The apparatus is shown in Fig. 5. *T* is the measuring vessel made of stout glass which ends in a carefully calibrated capillary tube. The lower part of the vessel is placed in a steel cylinder. By means of a brass piece A and a screw E the vessel is held in the steel cylinder. M is a thermostat surrounding the upper narrow part of the tube which is again closed by means of a mantle C. The vessel T is filled with the gas under investigation at atmospheric pressure, the space between T and the inner wall of B being filled with a sufficient quantity of mercury over which a quantity of glycerine or paraffin oil is poured. Pressure is communicated from a compression pump through glycerine to the measuring vessel. At high pressures the mercury will rise up to the capillary tube and the volume of the enclosed gas can be easily read off from the graduations. When the pressure is high, it is measured by a compression manometer. If the pressure is above 300 atmos. and is exerted

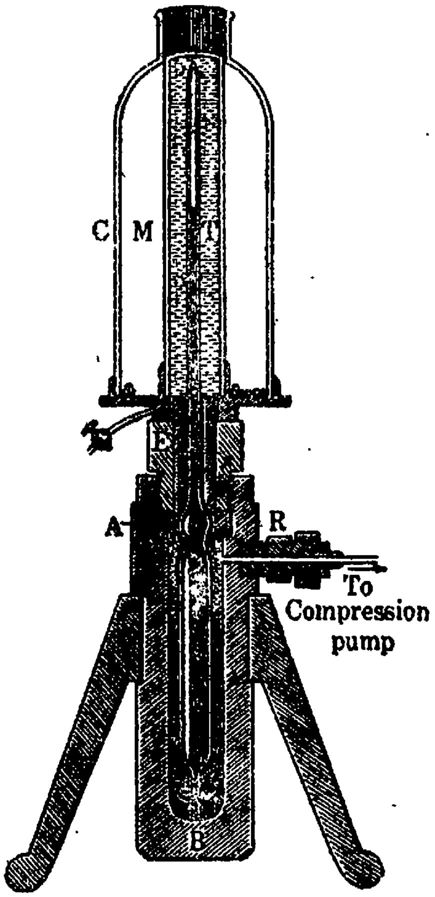

Fig. 5.—Cailletet's apparatus.

only from the inside the capillaries are generally smashed, hence the experimental tube must be subjected to pressure from all sides. Such a pressure tube was built by Amagat.[1]

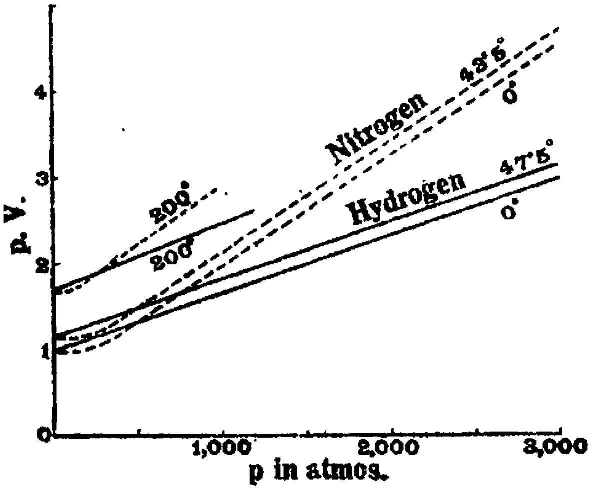

Fig. 6.—Amagat's curves (pV against p) for different gases.

Amagat carried out an exhaustive study of the behaviour of several gases by the above method. In one set of experiments he employed pressures up to 450 atmos. while in the next series pressures as high as 3000 atmospheres were used.[2] We shall now discuss his results.

Amagat represented his results by graphs in which pV denotes the ordinate and p the abscissa. The curves for hydrogen and nitrogen for several temperatures are shown in Fig. 6. As already

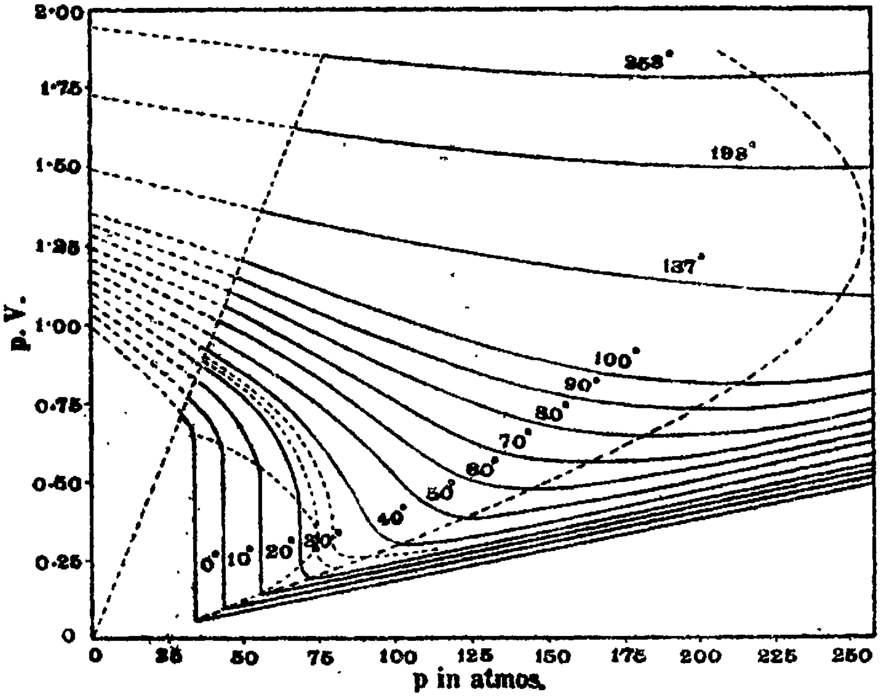

Fig. 7.—Isothermals for CO_2.

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[1] For a detailed description see Müller-Pouillets, *Lehrbuch der Physik*, Vol. 3, Part I, p. 242.

[2] A very good account of these experiments is given in Jellinek, *Physikalische Chemie*, Vol. I, pp. 334—354.

mentioned, for H_2 the product pV inceases with pressure, but for nitrogen it first decreases and then increases. The curves are straight lines *inclined* to the pressure-axis while if Boyle's law held true they would be straight lines *parallel* to the pressure-axis. The curves[1] for CO_2 (Fig. 7) are typical of all gases. The isothermals below about 30° have a portion of them parallel to the pV-axis. This indicates that the pressure remains constant while the volume varies, and corresponds to the condensation of the vapour. Further it is seen that the curvature of the isothermals diminishes as the temperature rises. The minima points on isothermals gradually recede away from the origin, and the dotted curve through them is roughly parabolic.

The general shape of this curve can be easily explained; for

$$\frac{\partial(pV)}{\partial p} = B + 2Cp + 3Dp^2 + \ldots,$$

and from what has been said on p. 397 regarding the variation of B and the values of $C, D\ldots$ it follows that the slope of these curves will be negative for low temperature and low pressure, and positive for high temperature with low or high pressures. This parabolic curve would meet the ordinate through $p = 0$ on an isothermal which will correspond to the Boyle temperature (for which $B = 0$). Above this temperature no minima points are found and carbon dioxide behaves like H_2. In fact all gases will behave like CO_2, only for H_2 these changes will occur at very low temperatures.

(*b*) As an example of apparatus employing the principle of constant volume which has been much employed by Kamerlingh Onnes,[2] we describe an apparatus due to Holborn and Schultze[3].

The experimental vessel A (Fig. 8) whose volume is accurately known, is placed inside a steel cylinder B. The latter can be subjected to the same pressure as the inside of A by opening the valves v_3, v_4, v_5 and v_2, v_6 and adjusting the levels in P_1 and P_2 to be the same. The vessel A is connected by means of a platinum capillary shown at '*a*' and the valves v_2, v_6 with the mercury pump P_1PP_2 which acts as a compression pump. On opening the valves v_6, v_7 the vessel A can communicate with a gas holder containing the gas under investigation which is connected at *e*. Compressed air from a steel flask can be forced through c_1, v_5 and v_4 into P_1 and drives the mercury out of P_1 to P_2. If now the mercury is allowed to pass from P_2 back to P_1 while the latter is connected by means of v_4 and c_2 to the atmosphere and the valve v_6 is kept closed, then simultaneously the experimental gas is sucked in at *e* and passes through v_7 into P_2 from which it can be transferred to the vessel A by closing v_7 and opening v_6 and c_2 and raising the pump P_1. Thus the mass of gas contained in A can be varied at will. The pressure is measured by the pressure balance D. The experimental results obtained by Onnes have already been discussed.

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[1] These curves can be fully understood and interpreted with the help of van der Waals' equation and will be found to show striking concordance with Andrews' curves.

[2] *Leiden Commun.*, Nos. **69**, **78**, **97**.

[3] *Ann. d. Physik*, **47**, 1089, 1915; *Zeits. f. Physik*, **40**, 320, 1924, and other papers.

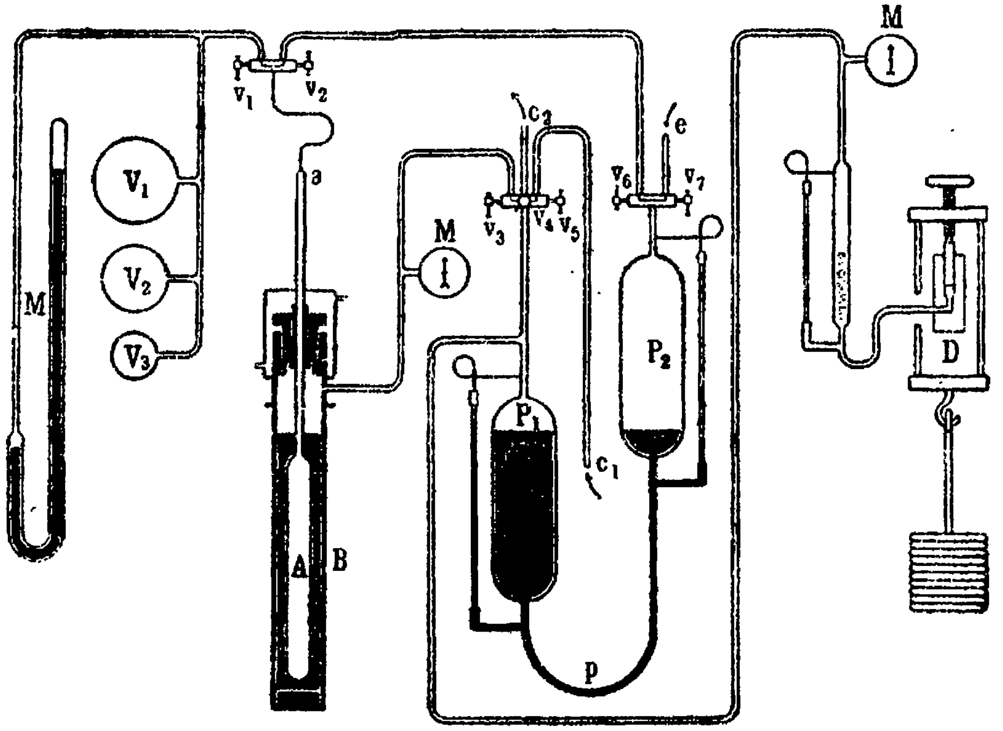

Fig. 8.—Holborn and Schultze's apparatus.

10·17. Experimental Determination of Critical Constants.—We have defined the critical constants in sec. 10 3. They are constants characteristic of every substance; and are of fundamental importance as they occur in certain equations of state. Their importance in the study of liquefaction is discussed in Chap. XII.

The determination of these critical values is often a task of considerable difficulty. Of these the *critical temperature* is the easiest to measure. For ordinary substances a hard glass tube like that of Andrews and connected to a manometer may be employed. Sufficient quantity of the liquid is introduced and the tube surrounded by a thermostat which can be maintained at constant temperatures differing by very small amounts. The temperature at which the liquid suddenly disappears[1] and reappears are observed, the mean of these giving the critical temperature. The *critical pressure* is the vapour pressure which is observed when the liquid just disappears and can be read easily from the manometer. The critical volume is much more difficult to measure accurately for even a small variation of temperature by 0·1°C may produce a large change in volume and hence the substance has to be kept exactly at the critical temperature. The pressure also must be exactly equal to the critical pressure since the compressibility of the substance in this region is very great. The method adopted was to arrange in such a way that a very slight increase of volume lowered the temperature by a small amount and caused the separation of the mass into liquid and vapour, the liquid appearing at the top[2]. This initial volume is called the *critical volume*. The amount of substance initially contained in the tube has to be thus adjusted.

The most accurate method, however, is to make use of the *Law of Rectilinear Diameters* or mean densities, discovered by Cailletet and Mathias[3]. If the density of a saturated liquid and of its saturated vapour be represented by ordinates and the corresponding temperatures by abscissa, a curve roughly parabolic in shape is obtained (Fig. 9). In the figure the vapour density of nitrogen is plotted from the observations of Onnes and Crommelin[1] and is typical of all substances. The densities in the two states go on approaching each other till they become equal at the critical temperature. The curve AB is a line passing through the mean of the vapour and liquid densities and will consequently pass through the critical temperature. It was first observed by Cailletet and Mathias that for all substances this line was straight or very nearly so[2]. The equation for this line is $y=\frac{1}{2}(\rho_l+\rho_v) = a + bt$, where y is the ordinate and t the abscissa, and ρ_l, ρ_v denote the densities in the liquid and the vapour states respectively. This law enables us to find the critical density or the critical volume, for we determine the densities of the saturated vapour and the saturated liquid as near to the critical temperature as possible, then draw the rectilinear diameter. The intersection of this line with the ordinate at the critical temperature gives the critical density ρ_c or the critical volume.

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[1] Recent investigations (see §10·18) show that the meniscus is not visible even at temperatures slightly lower than the critical when the properties in the liquid and gaseous phases have not yet become identical. Thus there is a small temperature interval over which the meniscus is invisible. Hence for accurate determination the properties of the liquid and vapour phase have to be found over a range of temperatures near the critical temperature and the temperature at which these properties become equal is taken to be the critical temperature (See Fig. 12 §10·18).

[2] This is the case when there is a slight excess of the substance in the vessel (see §10·18).

[3] *Comptes Rendus*, **104**, 1563, 1897; *Journal de Physique* (2), **5**, 549, 1886.

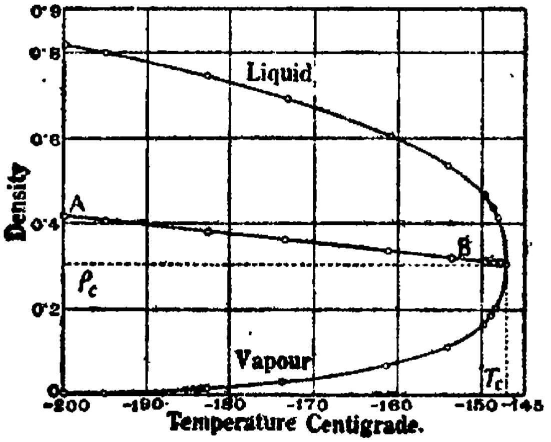

Fig. 9.—Law of rectilinear diameters.

For substances like water which attack glass at high temperatures Cailletet and Colardeau[3] employed the apparatus shown in Fig. 10. The strong steel tube AB, platinized inside to prevent attack, contains the water or the substance to be investigated. It is immersed in a temperature bath LL which is heated by a gas regulated burner, and thus its temperature can be kept constant. The tube AB is connected to a similar steel tube FG by means of the flexible steel spiral CDE. Mercury fills part of the tube AB, the spiral CDE and the tube FG up to the level S_1 above which there is water filling the entire tube upto the manometer M. Different pressures can be applied by the force pump as indicated. At S_1 an insulated platinum wire is sealed in the side of the wall and completes an electric bell circuit. When the temperature of the bath is raised, the pressure of the vapour in AB rises, mercury is forced past S_1 in FG and sets the bell ringing. Water is forced in by the pump to keep the level of mercury constantly at S_1 and thus the volume occupied by the water and water vapour in AB remains constant. The platinum wire at S_2 completes another electric circuit and serves to sound a warning that the whole mercury is about to be expelled out of AB.

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[1] *Leiden Commun.*, No. **145** (c).

[2] For some substances the line is not quite straight. See *Handbuch der Physik*, **10**, p. 171.

[3] *Comptes Rendus*, **112**, 56, 1891; *Ann. de Chemie et de Physique*, 6e, **25**, 519.

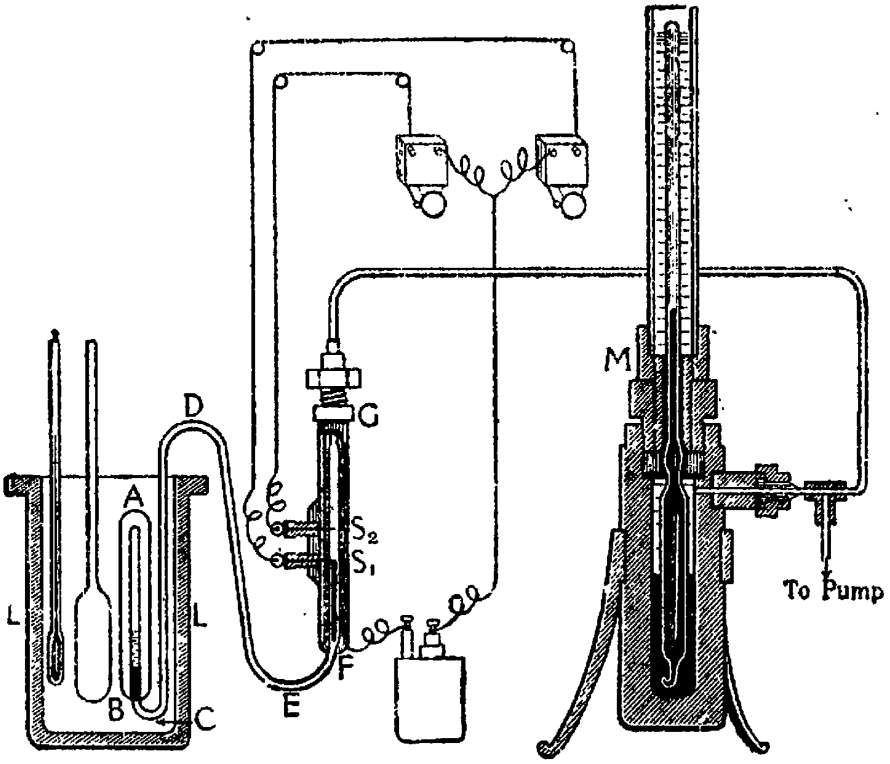

Fig. 10.—Cailletet and Colardeau's apparatus.

We thus get the vapour pressure curve of the substance. The curve is perfectly continuous and characteristic of the substance. For water this is shown in Fig. 11. If, however, we start with different quantities of the liquid we get the same curve as far as M, but above it we get different curves. The vapour pressure curve thus appears to branch off at M, a point whose position was found by Cailletet to be practically independent of the quantity of liquid taken. This temperature is the critical temperature for the substance.

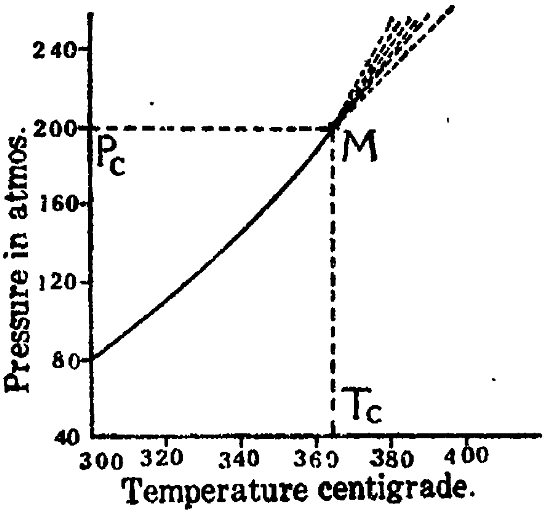

Fig. 11.—Vapour pressure curve for water.

We give below a table of critical constants, taken from Landolt and Börnstein's *Physikalisch-Chemische Tabellen.*

Table 4.—*Critical Data.*

Gas	T_c in °C.	p_c in atm.	specific volume v_c in c.c.	$\frac{RT_c}{p_cV_c}$
Helium	−267·9	2·25	15·4	3·13
Hydrogen	−239·9	12·8	32·2	3·28
Argon	−122·4	48	1·88	3·43
Oxygen	−118·8	49·7	2·32	3·42
Nitrogen	−147·1	33·5	3·21	3·42
Carbon dioxide ..	31·0	72·8	2·17	3·48
Ammonia	132·2	112·3	4·24	4·12
Ether	193·8	35·6	3·85	3·81
Sulphur dioxide ..	157·2	77·6	1·95	3·60
Methyl chloride ..	143·1	65·9	2·71	3·80

10:18. Matter Near the Critical Point.—There has been much discussion about the state of matter near the critical point since the time of Andrews. The properties actually observed are:—(1) the densities of the liquid and the vapour gradually approach each other till they become equal at the critical point; (2) at or very near the critical temperature the boundary line between the liquid and the vapour disappears, and hence there must be mutual diffusion, and the surface tension must vanish, *i.e.*, the molecular attraction in the liquid and vapour states must become equal; (3) the whole mass presents a very flickering appearance which suggests that there might be variations of density inside the mass. This was experimentally observed to be so by Hein[1] and others. They suspended spheres of different densities inside the fluid when each sphere comes to rest at a horizontal surface having a density equal to its own; (4) the compressibility of vapour at the critical point is infinite and is very great near the point. As pointed out by Guoy,[2] this explains the variation of density throughout the mass observed in (3), for the superincumbent vapour causes the density of lower parts to increase.

From these considerations the simplest and probably the most correct view which was put forward by Andrews appears to be that just beyond the critical temperature the whole mass is converted into vapour consisting of a single constituent and should behave like a gas near its point of liquefaction.

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[1] *Zeits. f. physik. Chemie*, **86**, 385, 1914.

[2] *Comptes Rendus*, **116**, 1289, 1893.

According to this theory the critical phenomenon, *i.e.*, the disappearance of the boundary between the liquid and the vapour and not its motion, should occur only when the amount of liquid in the tube is such that it will fill the whole tube with vapour of critical density. If more liquid is present the meniscus should go on rising till at the critical temperature the whole tube becomes filled with liquid. If less liquid is present, the meniscus goes on falling till at the critical temperature the whole tube should become filled with vapour alone. Experimentally, however, Hein[1] found that the critical phenomenon is observable when the initial density varies from 0·735 to 1·269 times the critical density. This is probably due to the property (4) as the variation of density inside the mass allows the excess or deficit amount to be adjusted. The branching of the vapour pressure curve at M observed by Cailletet and Colardeau may be explained in a similar way.

The experiments of Callendar,[2] however, throw a fresh light on the state of matter near the critical point. Using very pure water from which all traces of dissolved air had been carefully expelled, he found (see Fig. 12) that the densities of liquid and vapour did not become equal at 374°C, the temperature at which the meniscus vanished, but that a difference of density was perceptible even beyond that temperature and under favourable conditions could be traced up to about 380°C. The experiments were done in the following manner. The density of the liquid was accurately determined by taking different quantities of water sealed in tubes of quartz and noting the temperatures at which the meniscus just reached the top of the tube. Beyond 374°C this was found, though less accurately, by making similar observations on the line of demarcation between liquid and vapour which was visible due to difference of density.

The density of the saturated vapour was determined by using smaller quantities of liquid and observing the temperature at which the last trace of the liquid disappeared. This observation could not be extended beyond the critical temperature (374°C).

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[1] *loc. cit.* The paper contains full references on critical phenomena.

[2] *Proc. Roy. Soc. Lond.*, **120**, 460, 1928.

The results obtained by Callendar are shown in Fig. 12 which is self-explanatory. The experimental curve for the density of saturated vapour was produced beyond 374°C and was found to intersect the curve for water at about 380°C at which the densities become equal. This is in sharp contrast with the results of the simpler theory given above according to which the densities should become equal at the temperature at which the meniscus disappears. Callendar confirmed his results by drawing the total heat curves for water and saturated steam which were also similar and which showed that the latent heat at 374°C is not zero but is 72·4 calories per gram and vanishes at about 380°C. Above 374°C the liquid and vapour were found capable of mixing in all proportions and were in unstable equilibrium which could be easily disturbed by traces of impurities such as air. From this result it follows that under certain conditions some liquid does remain present up to some degrees beyond the point at which the meniscus vanishes. On this view the experimental observation of Hein cited above can be easily explained.

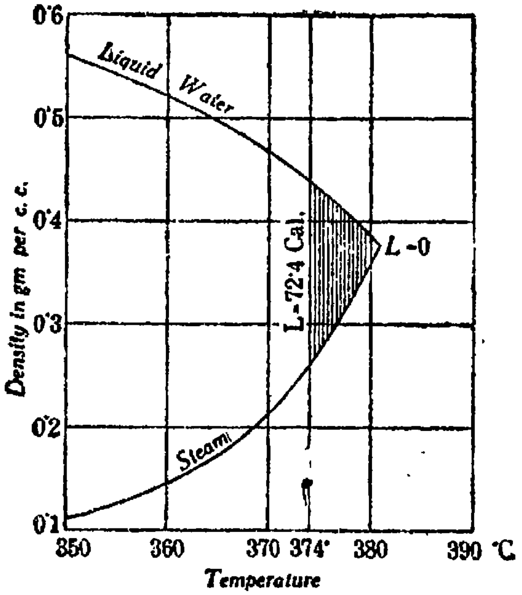

Fig. 12.—Density of water and saturated steam at different temperatures.

Thus we see that the disappearance of the meniscus, as was first thought, is not the criterion for the attainment of the critical point because it takes place through a range of temperature, pressure and density. *The critical point is that point at which the properties in the two phases become equal.* Similar results have been obtained by Maas[1] and his co-workers for propylene, ethylene and other substances. In their experiments a glass float was suspended by a quartz spring and immersed alternately in the saturated vapour and the saturated liquid with the help of a magnetically operated device from the outside. From the buoyancy and the consequent effect on the spring, the density could be calculated. For propylene he found that over an interval of about six degrees below the critical temperature the liquid and vapour densities differ so slightly that these two distinct phases with different densities cannot be distinguished visually and the meniscus between them has disappeared.

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[1] *Phil. Trans.*, **236**, 303, 1937.

Problems.

1. Show that the equation of Dieterici gives

$$V_c = 2b,\ p_c = \frac{a}{4e^2b^2},\ T_c = \frac{a}{4Rb},\ \frac{RT_c}{p_cV_c} = \tfrac{1}{2}e^2 = 3\cdot695.$$

2. Prove that for the Berthelot equation of state

$$V_c = 3b,\ p_c = \frac{1}{12b}\sqrt{\frac{2aR}{3b}},\ T_c = \sqrt{\frac{8a}{27Rb}}.$$

3. Using the formula

$$E = \frac{\lambda}{r^{12}} - \frac{\mu}{r^6}$$

for the intermolecular energy corresponding to the distance r, calculate the potential energy of a pair of He-atoms for different intermolecular distances and plot it as a function of r. Assume $\lambda = 0\cdot036 \times 10^{-104}$, $\mu = 11\cdot7 \times 10^{-61}$. What is the equilibrium distance r_0 for which the force vanishes ?

4. Using the law of intermolecular energy given in (3), calculate the second virial coefficient as a function of the temperature.

5. Calculate the thermodynamical functions F, G and H for a gas obeying van der Waals' equation.

Books Recommended.

1. Jeans, *Kinetic Theory of Gases*, C. U. P. (1940).
2. Jeans, *Dynamical Theory of Gases.*
3. Loeb, *Kinetic Theory of Gases* (1934), Chap. V.
4. Kennard, *Kinetic Theory of Gases* (1938).
5. R. H. Fowler, *Statistical Mechanics.*
6. Clemens-Schaefer, *Einführung in die Theoretische Physik*, Vol. 2.
7. Müller-Pouillets, *Lehrbuch der Physik*, Vol. 3, part I, Chap. 6.
8. *Handbuch der Physik*, Vol. X, Chap. 3.
9. Slater, *Introduction to Chemical Physics* (1939), published by McGraw Hill Book Co.

CHAPTER XI

CHANGE OF STATE (PHASE)

11·1. Fusion, Vaporisation, Sublimation, Phase Change.—It is a matter of common experience that on the application of heat, substances change their state of aggregation, passing generally but not always, from the solid to the liquid state, and from the liquid to the gaseous state. Let us illustrate by the commonplace example of water.

State :	Solid ⟶ Liquid	⟶ Gaseous
Process :	Fusion	Vaporisation
Temperature :	0°C.	100°C.
Pressure :	1 Atm.	1 Atm.

The temperatures at which these transitions take place are, however, not fixed, but depend on external pressure. It is common knowledge that liquid water can be made to boil at any temperature below 100°C., by sufficiently reducing the pressure. The dependence of the fusion-point on pressure is not so apparent, but it exists (vide p. 356). It has been found that ice can be melted at -1°C. by subjecting it to an external pressure of 130 atm.

Sublimation.—The solid may pass to the vapour state directly without passing through the liquid state. A common example is camphor, which, when slightly heated, passes directly to the vapour state without being liquefied. Such a substance is usually called 'Volatile', and the transitional process solid→vapour is called "*Sublimation*".

But it may be pointed out that '*volatility*' is not the characteristic property of any particular substance. All substances at sufficiently low temperatures may be solid, and give off vapour. Generally we confine the term 'volatile' to such solids whose *melting point* is higher than the boiling point at atmospheric pressure.

The "Atmospheric Pressure" is, however, not a fundamental quantity, but peculiar to our own planet only. If we are transported to another planet or satellite, say the moon, the "atmospheric pressure" will be extremely low, say fraction of a millimetre, and as the temperature is also very low, water will exist there only in the form of ice. If ice is heated in the moon, it passes straight to the vapour state, like camphor on the earth. If we want liquid water on the moon, we must heat ice under artificially created high pressure. Similarly, bodies which are volatile on Earth can be liquefied by heating them under high pressure.

Summarising the results we should say that all changes of state depend upon the two thermodynamical variables, *temperature and pressure.*

Latent Heat.—All changes of state at a fixed point also involve consumption of a large quantity of heat; a familiar example is ice at 0°C., which requires 79·6 calories of heat to pass to liquid water at 0°C. We have latent heats corresponding to fusion, vaporisation and sublimation.

Phase Changes.—Many substances in the solid state may, however, exist in different crystalline varieties, forming "different phases" according to the definition in §8·17, p. 360. An example is furnished by ice which, according to the experiments of Tammann and Bridgman, can exist in 'no less than seven different phases' which are stable under different ranges of temperature and pressure. This is shown in Fig. 1 and Table 1. (p. 444). Phase changes also involve consumption of heat (Latent heat of phase change).

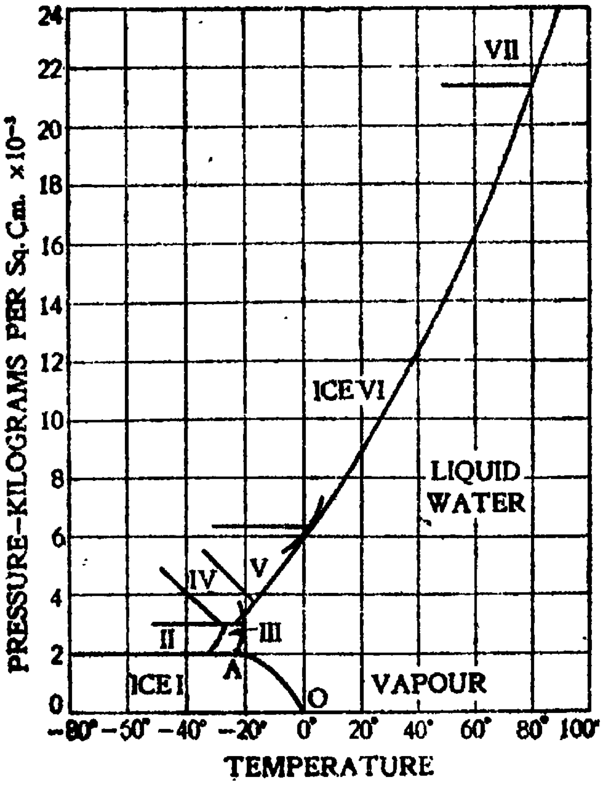

Fig. 1.—Phase diagram of water.

Table 1.—*Phases of Water and Triple Points.*

Phases in equilibrium	Pressure	Triple Point	Density	
				gm./c.c
Ice I, liq. vapour ..	4·579 mm.Hg.	+0·0098°C.	Ice I	0·92
Ice I, III, liq. ..	2115 Kg./cm.^{2}	–22°	Ice II	1·03
Ice I, II, III ..	2170 „	–34·7	Ice III	1·04
Ice II, III, V ..	3510 „	–24·3	Ice IV	
Ice III, V, liq. ..	3530 „	–17·0	Ice V	1·06
Ice V, VI, liq. ..	6380 „	+ 0·16	Ice VI	1·099
Ice VI, VII, liq. ..	22,400 „	+81·6		

The melting point of water is lowered by the application of pressure at the rate of 1° for 130 atmospheres (Curve OA). At –22°C. and $p = 2115$ Kg./cm^2 it can no longer be melted, but passes to variety II with the density 1·03. On release of pressure it lapses to ordinary ice. The effect of greater pressures is shown in Fig. 1. With the application of very great pressure, water can be frozen into ice, even above 0°C., as the curve (Ice VI, liq.) shows. When the pressure is above 25,000 Kg./cm^2, water can be frozen to ice even at 100°C. Probably the different forms of ice differ in their crystalline form, but these points do not appear to have been investigated.

The melting point curve of ordinary ice (Curve OA) is rather abnormal, due to the fact that the specific volume of ice is greater than that of water. Generally, specific volume in the solid state is less than in the liquid state and the curve has the form as shown in the curve (Ice VI, liquid). Vide Chap. VIII.

Substances in the liquid state also can exist in different phases e.g., Liquid Helium which at and below 2·19°K (Lambda point), can exist in two phases which have been called He I and He II (vide infra).

11·2. Change of Properties on Melting.—Several properties[1] of substances change in a very marked way when a substance melts. The following are among the important ones :

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[1] For a detailed discussion see *Handbuch der Physik*, Vol. X, pp. 70-80.

(1) *Change of Volume.*—Most substances expand on solidification while a few others contract. To the former class belong ice, iron, bismuth, antimony, etc., paraffin wax and most metals belong to the latter class. Good castings can only be made from substances which expand on solidification. Often enormous force is exerted by water when it freezes into ice. The bursting of water pipes and of plant cells and the splitting of rocks is due to this cause.

(2) *Change of Vapour Pressure.*—The saturation vapour pressure abruptly changes at the melting point. The vapour pressure curve of the solid and liquid states are different and there is a sharp discontinuity at the melting point.

(3) *Change of Electrical Resistance.*—The electrical resistance of metals undergoes a sudden change on melting. When the substance contracts on melting the conductivity increases and when it expands on melting the conductivity decreases. Table[1] 2 gives the ratio of the resistance of the fluid metal to that of the crystallised metal at the melting point for a number of metals.

Table 2.—The Ratio $\frac{\textit{resistance of fluid metal}}{\textit{resistance of crystallised metal}}$ *for some metals.*

Substance	Ratio	Substance	Ratio	Substance	Ratio
Al	1·65	Ga	0·58	Na	1·34
Sb	0·70	Au	2·28	Ag	1·98
Pb	2·06	K	1·39	Bi	0·45
Cd	1·97	Cu	1·97	Zn	2·00
Cs	1·65	Li	1·96	Sn	2·01

(4) It is also found that molten metals show a discontinuity in their power of dissolving gases at their melting point.

11·3. Determination of the Melting Point.—The melting point under normal conditions can be determined with very simple apparatus. The substance may be heated in a crucible electrically or otherwise. For high temperatures, the crucible must be of graphite or some other suitable material, and the substance heated in a non-oxidizing atmosphere. If the substance is rare, it can be employed in the form of a wire (wire-method). As thermometers, the secondary standards are very convenient to use, the thermocouple or the resistance thermometer being generally chosen; such thermocouples or resistance wires must not be thrust directly into the melting substance, but should be protected by a sheath of insulating material, say porcelain, hard glass or magnesia tubes. Now as long as the substance is melting the temperature remains constant and hence the E. M. F. of the thermocouple or the resistance of the thermometer is also stationary. A curve is plotted with the E.M.F. or the resistance as ordinate and time as abscissa. The horizontal part represents the freezing of the metal and the corresponding E.M.F gives its melting point. Such a curve for copper is shown in Fig. 2 where 90Pt-10Rh, Pt couple is used for measurement of temperature and the time is represented in minutes. The constant E.M.F. of the horizontal part is about 10·5 mV, which corresponds to 1084°C.

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[1] *Handbuch der Physik*, Vol. X, p. 73.

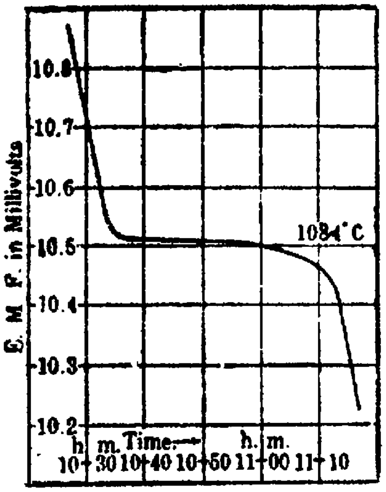

Fig. 2.—Melting Point of Copper.

Amorphous Solids.—Only crystalline substances have got a definite melting point, the amorphous substances have no such property. They merely soften on heating and pass gradually to a mobile state. Their viscosity diminishes and they become mobile. Such substances are not solids in the strict sense of the word, but are only supercooled liquids. To this class belong glasses, fats, wax, pitch, etc.

11·4. Latent Heat of Fusion.

—For determining the Latent Heat of Fusion ordinary calorimetric methods may be employed, *e.g.*,—(1) the method of mixtures, (2) the Bunsen ice calorimeter, (3) the method of cooling and (4) method based on the determination of the lowering of the freezing point when a measured quantity of a second salt, which dissolves in the molten mass, is added. The last method is indirect and will not be described here.

The method of mixtures.—It is quite simple and has been explained in §2·4. Most of the early determinations of the latent heat of ice were made by this method. If M grams of ice at 0°C. are added to a calorimeter containing water whose total thermal capacity is W and initial temperature θ_1 and if θ_2 be the final temperature, the latent heat L is given by the relation

$$ML+M\theta_2 = W(\theta_1-\theta_2). \quad . \quad . \quad . \quad . \quad (1)$$

An important source of error in the above method lies in the fact that some water adheres to the crystals of ice at 0°C. To eliminate this, ice below 0°C. is frequently chosen, but this procedure requires a knowledge of the specific heat of ice. In this method we are required to find the heat taken up by ice in being heated to 0°C. A converse method may also be employed, *viz.*, the heat given out by water on solidification may be found. The most accurate experiments give the value $L = 79{\cdot}6$ cal. for the latent heat of fusion of ice.

The method of mixtures has been very conveniently adopted to the simultaneous determination of the melting point and the latent heat of fusion of metals and their salts. Goodwin and Kalmus[1] employed this method for finding the latent heat of fusion of various salts. A known weight of the substance contained in a sealed platinum vessel is heated in an electric furnace to a high but accurately measurable temperature. It is then dropped into a calorimeter and the quantity of heat liberated is determined in the usual manner. The platinum vessel is cylindrical in shape and water-tight. The electric furnace is specially designed to secure a uniform temperature throughout the platinum cylinder which is measured by a Pt-Rh thermo-couple. As calorimetric liquid, water was employed below 450°C. while above that temperature aniline was used.

First a blank experiment gives the heat capacity of the platinum vessel. The experiment is then performed with the substance heated to different initial temperatures extending over a range of about 50°C. both above and below the melting point, and the final temperature of the calorimeter noted. From these, after correcting for the heat capacity of the vessel, the quantity of heat Q necessary to raise 1 gram of the substance from the room temperature to its initial temperature could be calculated. Plotting Q as ordinate and T the corresponding initial temperature as abscissa curves of the type shown in Fig. 3

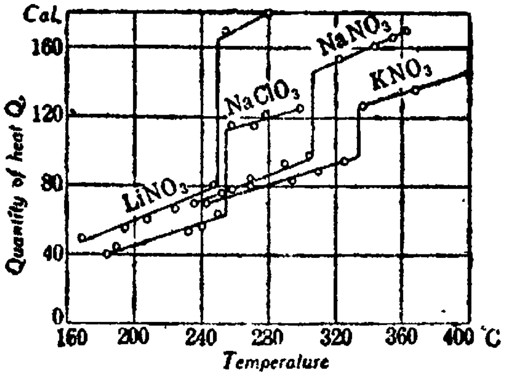

Fig. 3.—Latent Heat of Fusion of Salts.

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[1] *Phys. Rev.* I, **28**, 1, 1909.

are obtained. The discontinuity in the value of Q indicated by the vertical line gives the latent heat of fusion, the temperature at which this discontinuity appears is the melting point T_m, and the slope of the curve at any temperature gives the specific heat of the substance at that temperature.

This method has been considerably improved by Awbery and E. Griffiths[1] who have made accurate determination of the latent heat of fusion of several metals. They employed a very special type of calorimeter which was so designed that the heated substance could be kept surrounded by water inside the calorimeter and the lid of the latter closed before any water had access to it, so that the loss of liquid by evaporation was eliminated.

In this experiment, the quantity of heat which the substance could yield is measured by the method of mixtures. A *Bunsen ice calorimeter* may however be used for measuring that quantity of heat. The method is however not capable of great accuracy.

Method of Cooling.—Tammann and Jüttner,[2] and after them Plato, determined the latent heat of fusion from observation of the time required for complete freezing. The substance is heated above its melting point and the cooling curve determined. If t is the time required for complete freezing and dT/dt is the slope of the curve when freezing just started, then the latent heat

$$L = \text{Const.} \times t \times \frac{dT}{dt}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Electrical Method.—This consists in measuring the amount of electrical energy required to heat a mass of the substance below its melting point to a temperature above it. The method was employed by Dickinson, Harper and Osborne[3] for finding the latent heat of fusion of ice. Electrical energy was supplied to a special calorimeter similar to that of Nernst in which ice below 0°C. was placed. Then

$$E = \int_{T_1}^{T_m} c_{p_1} dT + L + \int_{T_m}^{T_2} c_{p_2} dT, \quad . \quad . \quad . \quad (3)$$

where E denotes the electrical energy supplied per gram, T_1, T_2 its initial and final temperatures, c_{p_1}, c_{p_2}, the specific heats of ice and water respectively and T denotes the melting point. From this relation L can be calculated. This method is very convenient for finding the latent heat at low temperatures.

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[1] *Proc. Phys. Soc. Lond.*, **38**, 378, 1926.

[2] *Zeits. f. anorg. Chem.*, **43**, 215, 1905.

[3] *Bull. Bur. of Stand.*, **10**, 235, 1914.

Methods similar to the foregoing can also be employed for finding the heat of transformation of one allotropic modification to another but we are not concerned with them here.

Equilibrium Vapour Pressure of Solids and Liquids

11·5.—The equilibrium vapour pressure or saturated vapour pressure (S. V. P.) of a substance, whether in the solid or liquid state, may vary enormously. Thus for water, one of the best studied of substances, the S. V. P. has been measured from 0°C, where it is 4·58 mm. of mercury (Fig. 4) to its critical temperature (374·2°C) where S.V. P. is 218 atmospheres or $1\cdot66\times10^5$ mm. of mercury. In case of many solids, S. V. P. may be so low as to be beyond the range of any experimental method ($<10^{-8}$ mm.)

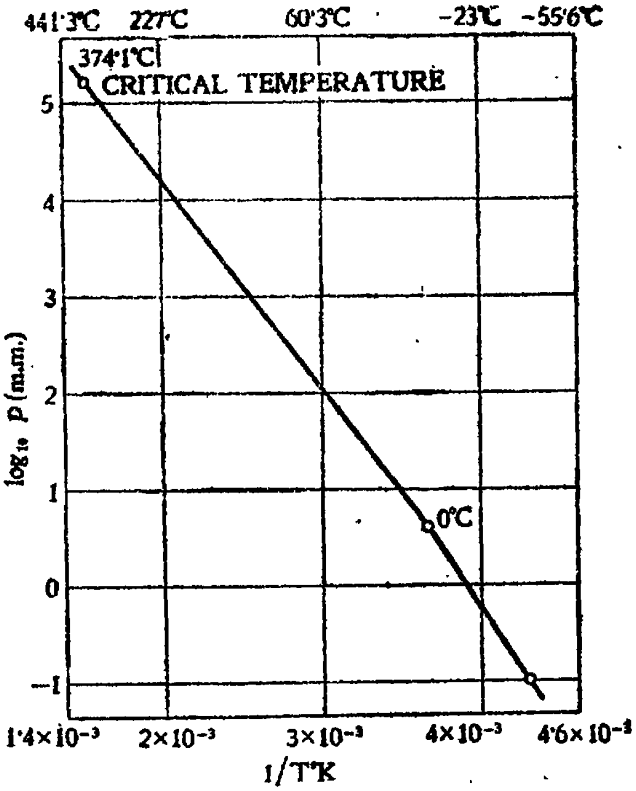

Fig. 4.—Vapour pressure curve of water.

On account of the enormous range to be traversed, a large variety of methods has been used which, following a report by Ditchburn and Gilmour (*Rev. Mod. Phys.*, **13**, 310) may be classified under the following categories. This report may be consulted for further reference.

I. High Pressure Methods (§11·6—11·7).
  (*a*) Direct manometric methods (static methods).
  (*b*) Boiling point and partial pressure methods (dynamic methods).

II. Low Pressure Methods (§11·8—11·9).
  (*a*) Effusion and allied methods.
  (*b*) Evaporation methods.
  (*c*) Manometric and electrical methods.

11·6. Static Methods.—As an illustration of the first method, (I*a*) we give a description of Regnault's apparatus, with which he determined the vapour pressure of water between 0°C and 50°C very accurately.

Two barometric tubes were arranged side by side, fed from the same cistern of mercury M. The space *a* above the mercury level in the tube B is vacuum while water is gradually introduced at the bottom of A till it rises through the mercury column and evaporates on reaching *b*. More water is introduced till a small layer remains floating over the mercury surface in A. A constant-temperature bath DD furnished with stirrer (not shown) and a thermometer surrounds *a*, *b*, as well as some length of the mercury column. The difference in the heights of the two mercury columns, which are observed through a glass window with the aid of a cathetometer, gives us the saturated vapour pressure of water at the temperature of the bath. Correction must be made for the weight of water in B, for effects of capillarity, refraction, etc.

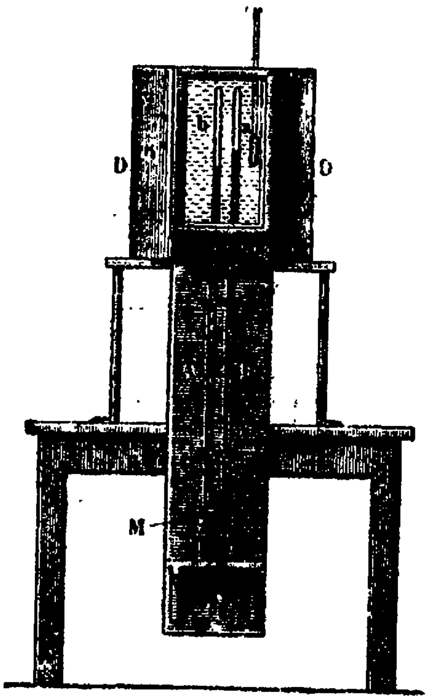

Fig. 5.—Regnault's vapour pressure apparatus.

For temperatures below 0°C, Regnault modified his apparatus to that of Gay Lussac. The top of the tube A was bent round and terminated in a spherical bulb which contained water or ice and was surrounded by a suitable bath. For temperatures not much above 50°C, the apparatus already described (Fig. 5) could be used when a longer bath would be necessary, but Regnault preferred the boiling point apparatus (Sec. 11·7).

This method can be used to find out the vapour pressure of any liquid provided it does not react with mercury and the vapour pressure is neither too high nor too low. Fig. 6 shows a general scheme of apparatus utilising this method, and is quite similar to the vapour pressure thermometer illustrated in Fig. 15, p. 40. A is a small glass sphere, a few c.c. in capacity, to which is attached a glass tube C and another glass tube D with a smaller bore. This is connected to a bigger globe G and a mercury manometer about 90 cm. long. The whole apparatus is first evacuated through the stop-cock S_1, and then the latter is closed. Next the gas under investigation is introduced through the stop-cock S_2 and condensed in A by suitably cooling the latter; finally

S_2 is also closed. The sphere A is then surrounded by temperature baths and the vapour pressure corresponding to the temperature of the bath is indicated by the manometer M. B is a barometer to indicate the atmospheric pressure. The apparatus is convenient for measuring vapour pressures from a few cm. to the atmospheric pressure. For higher pressures a compressed air manometer may be employed but the apparatus has to be made of steel.

This method has been used by Henning and Stock (*Zs. f. Phys.* **4**, 226, 1921) for finding the S. V. P. of a number of gases between 10° and −181°C., by Henning and Heuse (*Zs. f. Phys.* **23**, 113, 1924), and Heuse and Otto for the S. V. P. of a number of permanent gases, by Holborn and Baumann (*Ann. d. Phys.* **31**, 945, 1919) for S. V. P. of water above 200°C and by Smith and Menzies (*J. Am. Chem. Soc.* **43**, 547, 1921) and Jenkins (*P. R. S.* **110**, 456, 1926) for the same purpose. Isnardi and Gans (*Ann. d. Phys.* **61**, 267, 1920) modified the method by determining the vapour density ρ instead of p, and calculating p with the aid of the formula

$$p = \rho RT/M.$$

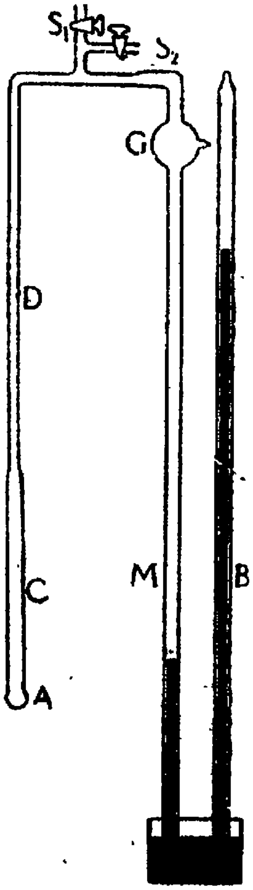

Fig. 6.—Determination of vapour pressure by statical method.

11·7. Dynamic or Boiling Point Method.—This method is based on the fact that when a liquid boils its vapour pressure equals the external pressure on the surface of the liquid. A definite external pressure is applied on the liquid surface by means of a pump and then the liquid heated in the presence of an inert gas which will not react with it. The liquid will boil at the temperature at which its vapour pressure equals the external pressure, *viz.*, that set up by the pump. Hence the vapour pressure corresponding to the temperature of ebullition is the pressure exerted by the pump and can be read on a manometer.

Regnault employed this method for finding the vapour pressure of water between 50°C. and 200°C. His apparatus is indicated in Fig. 7. The copper boiler A is partly filled with the experimental liquid and contains four thermometers *b*, *c* immersed to different depths inside the vapour and the liquid. The upper part of the boiler is connected to a large copper sphere G by means of a tube C which is itself enclosed in a water-cooling jacket D. The reservoir G is connected by means of H to a pump, the pressure being indicated by the mercury manometer NM. The reservoir is kept immersed in a water-bath W and serves to transmit the pressure from the boiler to the manometer as well as to smooth the fluctuations in the pressure maintained by the pump. The liquid condenses in C and returns to the boiler, thus the same quantity of liquid is used over and over again. First, a definite pressure is established by the pump and the boiler heated. In a short time the readings indicated by the thermometers *b*, *c* become steady. The manometer indicates the vapour pressure corresponding to this temperature.

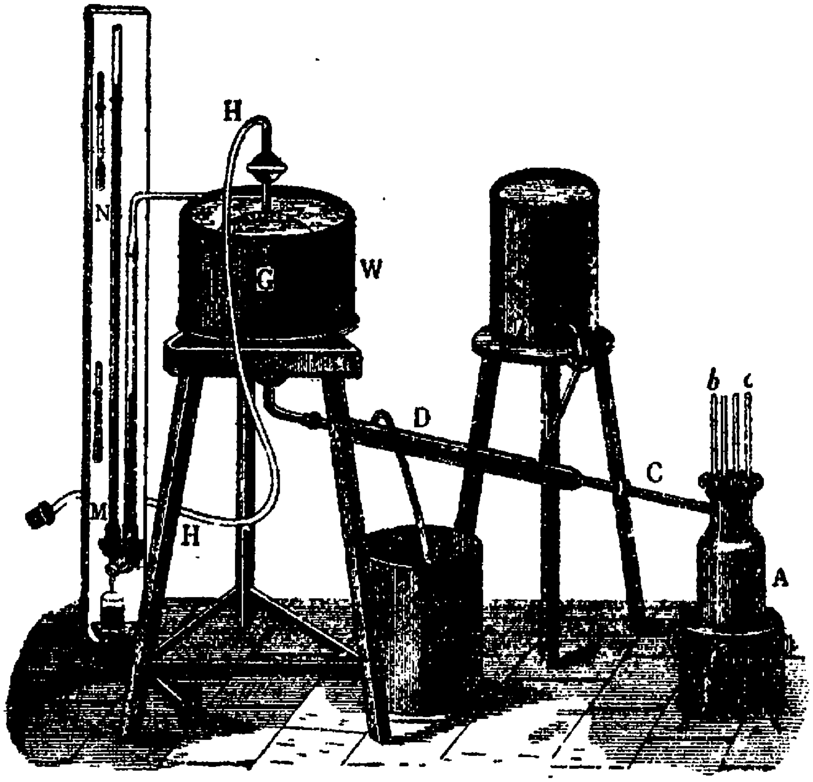

Fig. 7.—Regnault's vapour pressure apparatus (Dynamical method).

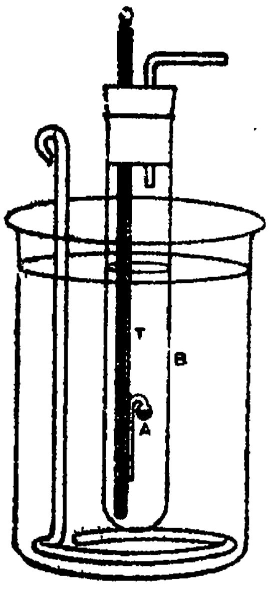

Fig. 8.—Smith and Menzies' apparatus.

The apparatus can be adopted for all pressures. For high pressure all the parts must be made of copper and the pump must be a force pump. Regnault used pressures varying from a fraction of an atmosphere to 28 atmospheres. The method is capable of great accuracy. By this method Holborn and Henning[1] have very accurately determined the vapour pressure of water between 50° and 200°C. (⅛ to 16 atmos.). Smith and Menzies[2] devised an ingenious modification of the dynamic method. Their apparatus is indicated in Fig. 8. The substance under investigation is kept in the sphere A close to the bulb of the thermometer T, both being immersed in some liquid contained in the test-tube B. The test-tube is closed air-tight and communicates with a pump and manometer (not shown). It is further surrounded by a bath whose temperature can be varied. A definite pressure is first established by the pump and the temperature of the bath gradually raised. When the vapour pressure of the substance contained in A becomes equal to the external pressure on the surface of the liquid in the tube, any further increase of temperature increases the pressure of the vapour in A which consequently bubbles through the liquid in the tube. When this just happens the pressure recorded by the manometer gives the vapour pressure corresponding to the temperature indicated by the thermometer.

The boiling-point method has also been applied to metals by Braun.[3] Zinc or cadmium was heated electrically in a quartz or porcelain tube and the temperature of the vapour was measured by a thermocouple. For interesting modifications, see Baur and Brunner, *Helv. Chim. Acta*, **17**, 958, 1934.

Low Pressure Methods

11·8. Effusion through a narrow opening.—This method is based on Knudsen's work[4] on the effusion of gases at low pressure, and is very simple and efficient particularly at low temperatures. We shall describe here the apparatus employed by Harteck.[5]

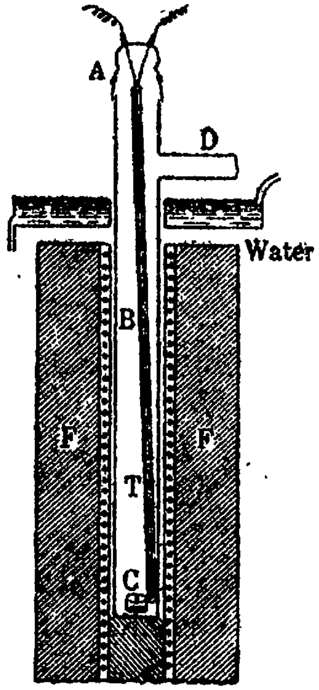

Fig. 9.—Vapour pressure by effusion.

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[1] *Ann. d. Physik*, **26**, 833, 1908.

[2] *Zeits. f. phys. Chem.*, **75**, 500, 1911; *Journ. Amer. Chem. Soc.*, **32**, 897, 907, 1448, (1910); *Ann. d. Physik*, **33**, 989, 1910.

[3] *Zeits. f. anorg. Chem.*, **2**, 119, 1920. [4] *Ann. d. Physik*, **91**, 179, 1900.

[5] *Zeits. f. Phys. Chem.*, **134**, 1, 1928.

Harteck's apparatus is shown diagrammatically in Fig. 9. The metal whose vapour pressure is to be determined is placed in a small quartz crucible C which has in its lid a hole of 1 to 3 mm. diameter. The crucible is placed at the bottom of a quartz tube B, 40 cm. high and 2 cm. in diameter, which stands with about 30 cm. of its length inside a chrome-nickel furnace FF. For temperatures above 1250°K. a platinum furnace of Heraeus is employed. The temperature of the crucible is measured by a platinum-rhodium thermocouple T whose junction is placed very close to the crucible. The quartz tube is closed at the top by a cap A through which the thermocouple leads are taken inside, and has a side-tube D for connection to the high vacuum pump. The cap and soldered junctions are cooled by water. The thermocouple is protected from the metal vapour by a thin quartz tube.

The experiment is done as follows :—The crucible with the metal is weighed before the experiment and then placed inside the quartz tube. Harteck first evacuated the tube B and then allowed the current to heat the furnace, and tried to obtain the desired temperature as quickly as possible. In his experiments this temperature was only approximately reached in about 25 minutes and became steady in some cases only after an hour. Then this temperature was maintained steady for about 2 to 36 hours, the fluctuations being less than 2°C. The metal vapour passed through the opening in the crucible and was condensed on the cooler parts of the apparatus. Finally the apparatus was cooled and the crucible again weighed. The loss in weight of the crucible gives the weight of the metallic vapour escaping through the hole. An expression for the same can be obtained from the kinetic theory in terms of the area of the hole and the vapour pressure of the metal inside the crucible.

The mass w of vapour escaping out of the hole in t seconds is from equation (100), p. 193, given by

$$w = \tfrac{1}{4}\bar{v}(\rho - \rho')At, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where A is the area of the hole, $\bar{v}$ the mean velocity and ρ, ρ' the densities of the metallic vapour inside the crucible and the tube respectively. ρ' is almost equal to zero since B is highly evacuated and further all the molecules of the vapour escaping out of the hole are immediately condensed. Again from the kinetic theory

$$\bar{v} = \sqrt{\frac{8RT}{M\pi}}, \quad \rho = \frac{M}{V} = \frac{Mp}{RT} \quad . \quad . \quad . \quad (5)$$

Substituting these values in (4) we get

$$w = At.\, p\sqrt{\frac{M}{2\pi RT}} \quad . \quad . \quad . \quad . \quad (6)$$

Hence the vapour pressure p of the substance at the temperature T is given by

$$p = \frac{w}{At}\sqrt{\frac{2\pi RT}{M}} \quad . \quad . \quad . \quad . \quad (7)$$

Thus knowing w, t, T and measuring A, the vapour pressure can be determined. Harteck found A by measuring the dimensions of the hole with a good microscope, while Egerton took a photographic impression of the hole, enlarged it several times and finally got a print on paper. He found the area of the print by counting the number of squares and knowing the magnification, the area of the hole was calculated.

Some corrections are however necessary. In Harteck's procedure, for part of the time at the beginning, the effusion took place at a lower temperature. To correct for this he observed the temperature at regular intervals and ascertained graphically the necessary correction which was only a few per cent. Egerton, on the other hand, first introduced hydrogen into B, then heated the furnace till the steady temperature was attained, and then quickly pumped off the hydrogen. The time of commencement of the experiment was arbitrarily taken as the instant at which the pressure of hydrogen in B was reduced to 1/20 mm. Further equation (7) requires correction since the silica tube B also offers a resistance W_r (see p. 202). This is given by

$$W_r = \frac{3}{4}\,\frac{1}{\sqrt{2\pi}}\,\frac{l}{r^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where l is the length from the hole to the point where the vapour deposits, and r is the average radius of the tube. This correction amounts to only about 1 per cent for the size of silica tube employed.

The method is sensitive to about 10^{-5} mm. of mercury. The upper limit is about 10^{-2} mm.

11·9. Vapour Pressure from the Rate of Vaporization.

—Langmuir[1] devised an ingenious method for finding the vapour pressure of substances which volatilize with difficulty such as tungsten, molybdenum, platinum, etc., and which cannot therefore be conveniently treated by Knudsen's method. He investigated the rate of evaporation from filaments of these metals in vacuum and from this he could calculate the vapour pressure of these substances.

The experiment was done in the following manner. A thin filament of the experimental substance about 0·01 cm. in diameter and 10 cm. or more in length is first weighed on a delicate micro-balance and then supported in the form of a loop inside an electric bulb. The bulb is carefully exhausted so that the pressure inside it is less than 0·001 mm. of mercury. The wire is heated by an electric current and kept at a constant temperature for about 30 minutes or so. Langmuir determined the temperature optically (see Chap. XV). The temperature was kept constant by keeping the product (voltage $\times \sqrt[4]{\text{current}}$) constant. During the heating, the molecules of vapour are emitted from the filament and get deposited on the walls of the bulb since at these low pressures the mean free path is very large. The heating is then stopped, the bulb broken open and the filament wire again weighed. From the loss in weight[1] the rate of evaporation and thence the vapour pressure can be calculated.

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[1] *Phys. Rev.*, **2**, 327, 1913; Langmuir and Mackay, *Phys. Rev.*, **4**, 377, 1914; Jones, Langmuir and Mackay, *Phys., Rev.*, **30**, 201, 1927.

The theory of the experiment can be easily worked out. As mentioned in Sec. 8·1, the equilibrium between a liquid and its vapour is dynamic, *i.e.*, at the surface of separation, the amount of liquid evaporated per unit surface per second is equal to the amount of vapour condensed on unit area per second. This will hold even if the vapour pressure is small and may be extended to the equilibrium between solid and vapour as well. Now from the Kinetic Theory of Gases the amount of vapour condensed depends upon its pressure and temperature. Again at temperatures such that the vapour of a substance does not exceed a millimetre of mercury we may safely assume that the rate of evaporation of the substance is the same whether it is in contact with its saturated vapour or placed in high vacuum. Hence the amount of the substance evaporated in high vacuum per second from unit area of the filament, *i.e.*, the rate of vaporization of the filament, must be equal to the amount of vapour that would be deposited in a second on unit area of surface placed in contact with saturated vapour. The latter can be easily calculated from the kinetic theory.

As on p. 454, the mass of vapour w striking unit area of surface per second is (from equation 7) given by

$$w = p\sqrt{\frac{M}{2\pi RT}}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where p is the required vapour pressure.

---

[1] The loss in weight can also be found by finding the change in electrical resistance but this yields less accurate results.

Langmuir and his coworkers assume that all the molecules striking the surface are absorbed by it, *i.e.*, Maxwell's factor f is unity. This assumption has been criticised by Harteck[1] and others and is open to doubt[2]. It appears probable that for metals in contact with their own saturated vapour f will be nearly equal to unity and Langmuir appears to confirm it from his experimental results because the value of λ_0, the molar latent heat at absolute zero, which he calculates on the basis of this assumption from observations at different temperatures, are fairly concordant. With this assumption[3] the rate of evaporation[4] per unit area of the filament will be given by equation (9).

The rate of vaporization can be easily determined experimentally. The mass m of the wire at any instant is given by $m=\pi r^2\rho$, where r is the radius of the wire and ρ denotes its density. Hence the radius of the wire is given by $r=\sqrt{m/\pi\rho}$.

Now the mass of metal lost by evaporation from unit length of the filament is $w.2\pi r$, and this should be equal to $-2\pi r\rho\, dr/dt$, where $-dr/dt$ denotes the rate at which the radius of the wire is decreasing. Hence

$$-2\pi r\rho\frac{dr}{dt}=w.2\pi r,$$

or

$$-\frac{dr}{dt}=\frac{w}{\rho} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and is constant. Therefore

$$\frac{w}{\rho}=\frac{r_0-r_1}{t}=\frac{\sqrt{m_0}-\sqrt{m_1}}{t}.\frac{1}{\sqrt{\pi\rho}}$$

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[1] *Zeits. f. phys. Chem.*, **128**, 1, 1925.

[2] For a full discussion of this point See Loeb, *The Kinetic Theory of Gases* (1934), Chap. VII, sec. 81.

[3] Equation (9) gives the maximum rate of vaporization. The actual rate of vaporization is somewhat less than this. Let it be given by $w=\alpha p\sqrt{M/2\pi RT}$. Then α is called the *vaporization coefficient*. Theoretically we see that for equilibrium in case of reflection of molecules $w=fp\sqrt{M/2\pi RT}$. Thus with our notations and assuming the theoretical considerations to be correct $\alpha=f$. Hence in case of reflection the actual vapour pressure will be greater than the vapour pressure obtained by equation (9) and can be obtained by dividing the latter by the fraction f.

[4] From equation (9) it follows that the rate of evaporation is $\propto\sqrt{M}$, or the number of molecules vaporized per second is $\propto\sqrt{M}/M=1/\sqrt{M}$. Hence substances having different molecular weights evaporate at different rates. This principle has been utilised by Bronsted and Hevesy in the separation of isotopes of mercury (see *Phil. Mag.*, **43**, 31, 1922).

or
$$w=\sqrt{\frac{p}{\pi}}\cdot\frac{\sqrt{m_0}-\sqrt{m_1}}{t}, \qquad . \quad . \quad . \quad . \quad . \quad (11)$$

where r_0, r_1 and m_0, m_1 denote respectively the radius and mass of unit length of the wire initially and after a time t. Thus knowing w from (11) the vapour pressure p can be calculated with the help of (9).

In Table 3, we give some results obtained by Langmuir and his co-workers. The values above about 3000° have been obtained by extrapolation. From this table we see that the boiling point of tungsten is 6970°K because at this temperature the vapour pressure is equal to one atmosphere. Similarly the boiling points of Mo and Pt were found to be approximately 5960° and 4800°K respectively.

Table 3.[1]—*Rate of evaporation and vapour pressure of of tungsten.*

Temp. °K	Evaporation per sq. cm. per sec. in gm. w	Vapour pressure in dynes/cm.^{2}	Temp. °K	Evaporation per sq. cm. per sec. in gm. w	Vapour pressure in dynes/cm.^{2}
1200	$3{\cdot}22\cdot10^{-27}$	$1{\cdot}58\cdot10^{-22}$	2800	$1{\cdot}12\cdot10^{-7}$	$9{\cdot}99\cdot10^{-3}$
1400	$2{\cdot}50\cdot10^{-22}$	$1{\cdot}57\cdot10^{-17}$	3200	$6{\cdot}67\cdot10^{-6}$	$8{\cdot}06\cdot10^{-1}$
1600	$1{\cdot}24\cdot10^{-18}$	$8{\cdot}61\cdot10^{-14}$	4000	$1{\cdot}7\cdot10^{-3}$	$1{\cdot}8\cdot10^{2}$
1800	$9{\cdot}46\cdot10^{-16}$	$6{\cdot}75\cdot10^{-11}$	5000	$1{\cdot}0\cdot10^{-1}$	$1{\cdot}2\cdot10^{4}$
2000	$1{\cdot}75\cdot10^{-13}$	$1{\cdot}32\cdot10^{-8}$	6000	$1{\cdot}3$	$1{\cdot}7\cdot10^{5}$
2400	$4{\cdot}36\cdot10^{-10}$	$3{\cdot}52\cdot10^{-5}$	6970	$7{\cdot}1$	$1{\cdot}0\cdot10^{6}$

The dynamical method has been employed by von Wartenburg[2] to determine the vapour pressure of lead, silver and thallium by passing an inert gas over the heated metal and measuring the concentration of the metallic vapour in the gas.

The manometric and electrical methods are also sometimes employed. For the latter purpose Pirani gauge (Chap. III) may be used.

11·10. Vapour Pressure of Solutions.—It was early observed that the saturated vapour pressure over a solution is always less than that of the pure solvent. In fact it can be shown from theoretical considerations that for dilute solutions the lowering $\triangle p$ of vapour pressure when a non-dissociating solute is added to a solvent, is given by the relation[1]

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[1] Taken from *Phys. Rev.*, **30**, 211, 1927.

[2] *Zeits. f. Electrochemie*, **19**, 482, 1913; Thiele, *Ann. d. Physik*, **14**, 937, 1932.

$$\frac{\triangle p}{p} = \frac{n}{N}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

where n is the number of molecules of the solute and N that of the solvent. The experimental methods for the measurement of the lowering of vapour pressure are described below.

The vapour pressure of solutions was determined by Faraday, Tammann, Raoult, Walker; Beckmann, Menzies and others. Tammann measured vapour pressure at 100°C. by observing the decrease of external pressure required to make the liquid boil at that temperature. Raoult[2] determined it by introducing the solution into the Torricellian vacuum of a mercurial barometer as in Regnault's experiment and observing the depression of the mercury column The lowering of the vapour pressure was found by comparing with another similar barometer in which pure solvent had been introduced. As a result of his experiments Raoult gave the law of lowering of vapour pressure, viz., *the relative lowering of vapour pressure is equal to the mole fraction of the solute and is independent of temperature and also of the nature of the solvent and the solute.* For dilute solution this law reduces to the form given in equation (12). Ostwald and Walker's[3] method consists in passing a current of dry air first through the solution, then through the pure solvent and lastly over pumice moistened with sulphuric acid. The relative lowering of the vapour pressure is obtained by dividing the loss in weight of the pure solvent by the gain in weight of the pumice. Menzies[4] has devised a simple apparatus in which the difference in the two pressures is directly read.

None of the direct methods so far developed is capable of any great accuracy. Accurate vapour pressure data of solutions, however, have great thermodynamical importance and hence, methods have lately been developed for precise measurements of vapour pressure of solutions of which the *isopiestic vapour pressure method of* Robinson[5] is the most important. This method in principle consists in allowing the test solution to come in thermodynamic equilibrium with a solution, whose vapour pressure is already known by enclosing both of them in a closed space at constant temperature and letting distillation from the solution of higher vapour pressure to that of lower vapour pressure to continue until equilibrium is reached. This method is extensively used now-a-days.

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[1] For a deduction of this on the basis of the kinetic theory see Müller-Pouilet, *Lehrbuch der Physik*, Vol. 3, Part 2, p. 310.

[2] *Compt. Rend.*, **103**, 1125, 1886.

[3] *Zeits. f. phys. Chem.*, **2**, 602, 1888. [4] *Ibid.*, **76**, 231, 1911.

[5] Robinson and Sinclair, *J. Amer. Chem. Soc.*, **56**, 1830, 1934.

Of the indirect methods the boiling point method and the freezing point method are capable of a fair degree of accuracy and are extensively used for moderately precise results. Since the vapour pressure of the solution is lower than that of the pure solvent it is obvious that the solution must be heated above the boiling point of the solvent in order to make it boil, for only then its vapour pressure will be equal to the external pressure. Van't Hoff showed that the elevation $\triangle T$ of the boiling point is connected with the lowering $\triangle p$ of the vapour pressure by the relation

$$\frac{\triangle p}{p} = \frac{\lambda}{RT^2}\triangle T, \qquad . \quad . \quad . \quad . \quad . \quad (13)$$

where λ is the molar latent heat and T the boiling point of the pure solvent. Thus knowing $\triangle T$, $\triangle p$ can be calculated.

The same equation (13) also holds true for freezing point depression caused by a solute when dissolved in any solvent, where λ is the molar latent heat of fusion and T is the freezing point of the pure solvent.

Beckmann developed the apparatus for determining the elevation of the boiling point, a common form of which is shown in Fig. 10. The solution is contained in the inner tube A and the pure solvent in the outer concentric cylinder B. Both the vessels are provided with Leibig condensers and have glass beads placed in their bottom. The inner tube contains a Beckmann thermometer and has a thick platinum wire sealed into the bottom. The solution in this tube is thus heated by the vapour of the pure solvent surrounding it and the stationary temperature on the thermometer gives the boiling point of the solution. Beckmann's apparatus has since been im-

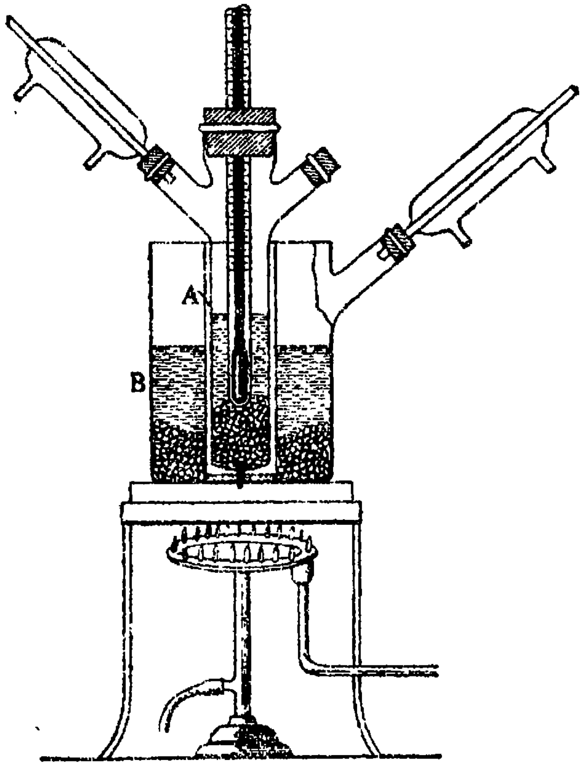

Fig. 10.—Beckmann's boiling point apparatus.

proved upon by other workers, the most common one having a fair degree of accuracy being that by Cottrell, for a description of which the reader is referred to any text book of physical chemistry.

Boiling point elevation in general, however, admits of less precision than freezing point depression measurements and so the latter are more generally used. The most widely used apparatus is that due to Beckmann which is shown diagrammatically in Fig. 11. It consists essentially of a test tube provided with a side tube for the introduction of the solid and is fitted with a rubber cork through which passes a stirrer and a Beckmann thermometer. The whole is supported in another large tube wide enough to provide an air mantle between the freezing tube and the outermost beaker which latter contains the freezing mixture. This ensures slow cooling and hence reduces chance of supercooling. The freezing points of the solvent and the solution are separately determined from which the depression $\triangle T$ of the freezing point is known. From the results of experiments with the above apparatus equation (13) has been amply verified for dilute solutions of non-electrolytes for both elevation of boiling point and lowering of freezing point.

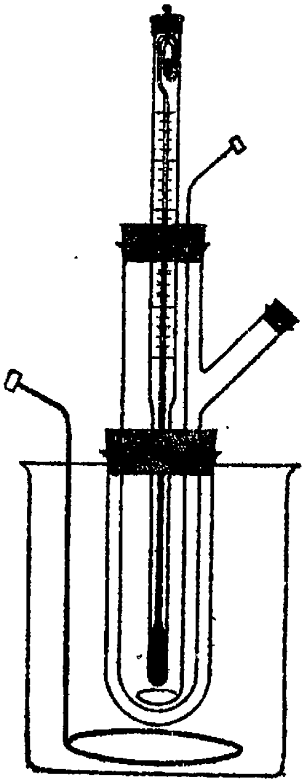
Fig. 11.—Beckmann's freezing point apparatus.

LATENT HEATS OF VAPORIZATION AND SUBLIMATION

11·11. In the measurement of latent heat of vaporization we have to remember two points, first, that its absolute value is relatively high; secondly, that the latent heat is absorbed or evolved in an isothermal change of state. The consequence is that its experimental determination is very little affected by the usual sources of error which are present in all calorimetric measurements. The methods can be grouped under three broad headings :

(A) *Condensation Methods.*—Those in which the amount of heat evolved when a certain amount of vapour condenses is measured.

(B) *Evaporation Methods.*—Those in which the amount of heat required to vaporize a given mass of the liquid is measured directly. The heat is generally added in the form of electrical energy and can be easily determined.

(C) *Indirect Methods.*—Those in which the latent heat is calculated with the help of certain thermodynamical relationships such as Clausius-Clapeyron relation (§7·2 and 8·12). The first method is historically the oldest.

11·12. Condensation Methods.—Regnault's experiments are rather of historical interest. We describe below the apparatus of Berthelot (Fig. 12). In this apparatus which is wholly of glass the liquid is kept in the vessel D and heated by the ring burner B. The rest of the apparatus is protected by an insulating plate M. The evaporated gas passes through the tube T into the spiral S placed within the calorimeter C. The spiral S is fitted to T by a conical ground piece and can be easily removed. The vapour condenses within the spiral and gives off its latent heat of vaporization to the calorimeter which can be easily measured by the rise of temperature on a thermometer placed inside the calorimeter. The calorimeter is placed inside a water jacket. The amount of water condensed is obtained by weighing the spiral S before and after the experiment. The heat measured represents the heat of vaporization plus the heat given up by the condensed liquid in cooling from the boiling point to the final temperature of the calorimeter. The open end of S is connected to a pump to regulate the pressure under which the boiling takes place.

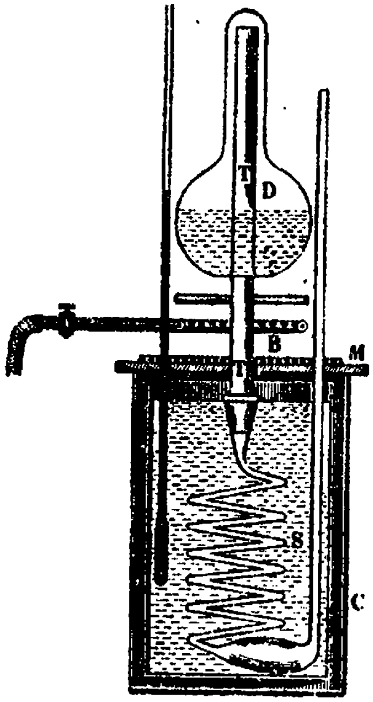

Fig. 12.—Berthelot's Latent Heat apparatus.

Errors are likely to arise owing (1) to superheating of the liquid, (2) to the minute drops of water being carried over by the vapour. The use of a ring burner causes the heating to be sometimes irregular. Kahlenberg[1] replaced the ring burner by a metallic spiral placed inside the liquid and heated electrically. Trautz and Dechend[2] used an electrically heated wire as a boiling accelerator. Richards and Mathews[1] placed the upper part of the apparatus within a Dewar flask maintained at a constant temperature. The part between D and the spiral was made as short as possible to prevent condensation of steam in the connecting tube TT.

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[1] *Journ. Phys. Chem.*, **5**, 215, 1901.

[2] *Zeits. f. Electrochemie*, **14**, 275, 1908.

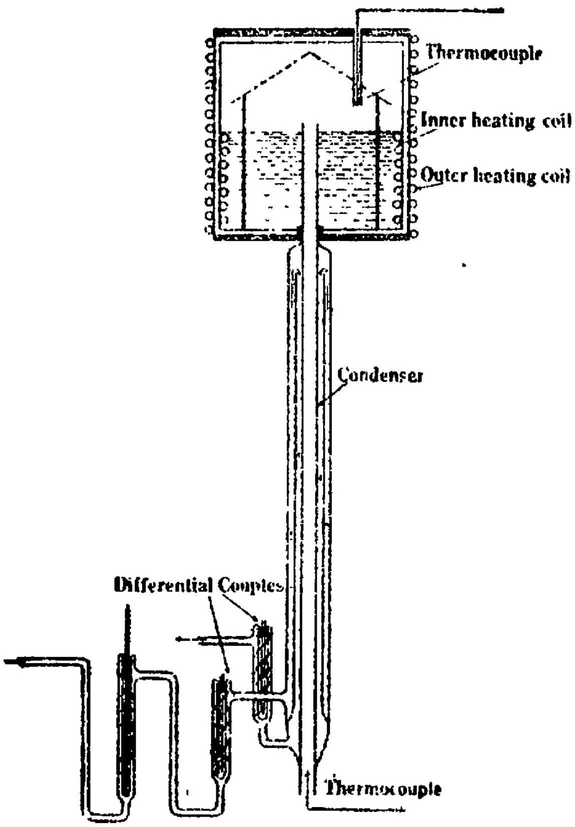

Fig. 13.—Awbery and Griffiths' Latent Heat apparatus.

Awbery and Griffiths[2] used a slightly modified apparatus in which the usual calorimeter was replaced by a continuous-flow calorimeter. The apparatus is shown in Fig. 13. The boiling chamber is heated electrically by an inner coil. The vapour passes down the vertical tube which is surrounded by a jacket of water through which a stream of water flows at a constant rate. The temperatures of the inflowing and outflowing water are determined by two thermocouples. There is a third thermocouple at the mouth of the vertical tube which gives the temperature of the condensed liquid as it leaves the apparatus. In this experiment the vapour must be produced at a steady rate and this is achieved by the use of electrical heating. The latent heat is obtained from the formula

$$M\theta = m[L+s(t_2-t_1)], \quad . \quad . \quad . \quad . \quad (14)$$

where θ is the excess of temperature of the outflow water over that of the inflow water, M is the quantity of water flowing per unit time, m is the rate at which the liquid is being distilled, t_2 is the boiling point of the liquid, t_1 the temperature of the liquid as it leaves the apparatus.

11·13. Evaporation Methods.—This method was employed by Dieterici[3] who measured the heat required to evaporate a given mass of water with the help of a Bunsen ice-calorimeter. The water was contained in the tube A of the ice-calorimeter (Fig. 6 p. 60) and the required quantity of heat was measured by finding the mass of mercury expelled. Griffiths[1] found the electrical energy required to vaporize a given mass of water. We shall describe the apparatus used by Henning[2] for precision measurement of the heat of vaporization between 30° and 100°C.

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[1] *Journ. Amer. Chem. Soc.*, **33**, 863, 1911.

[2] *Proc. Phys. Soc. Lond.*, **36**, 305, 1924.

[3] *Wied, Ann.*, **37**, 506, 1898.

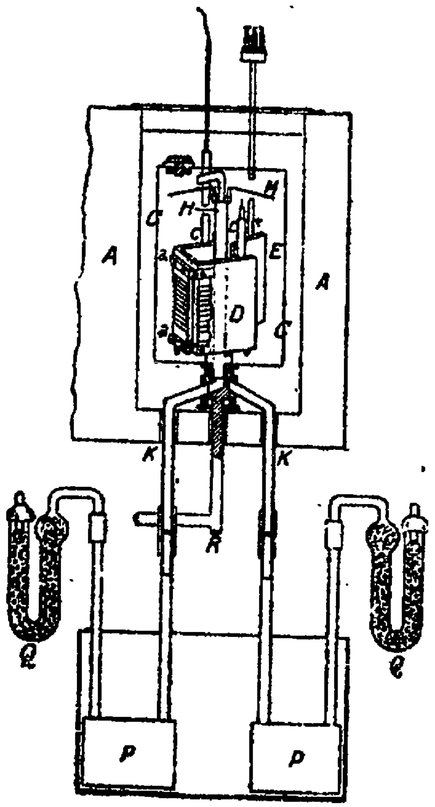

Fig. 14.—Henning's Latent Heat apparatus.

Henning's Experiments. — The apparatus employed by Henning is indicated in Fig. 14. C is a copper vessel, one litre in capacity, in which the liquid is allowed to evaporate. This is surrounded by an oil-bath A maintained at a constant temperature. The heating takes place through the spiral D of constantan wire wound on a quadrilateral mica frame. E is a platinum resistance thermometer. The vapour which is evolved passes through the German silver tube H downwards through the German silver tube KK to the vessel P in which it is condensed and weighed. The end of H is bent downwards so that no liquid drops can be carried. By turning the stop-cock R the vapour can be turned to any one of the vessels P, P. The vapour is at first led to one of the vessels P, and when the conditions become steady the stop-cock R is turned, and steam is led to the other vessel P. After a sufficient quantity of steam has been led to P the stop-cock R is turned to the other side.

The quantity of vapour deposited in the second vessel is now found by weighing and the quantity of heat supplied is obtained from observations of the electrical measuring apparatus. For determining the heat of evaporation at lower pressures P is connected to a large vessel of about 5 litres capacity which is maintained by means of a water-pump at the required pressure.

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[1] *Phil. Trans.*, p. 261, 1895.

[2] *Ann. d. Physik*, **21**, 849, 1906; **29**, 441, 1909.

A similar apparatus was employed by Henning[1] for finding the heat of vaporization of water up to 180°C when the pressure reaches about 10 atmospheres. Smith[2] employed a current of air for the evaporation of water. Fogler and Rodebush[3] used this method for determining the latent heat of evaporation of mercury up to 200°C.

For determining the latent heat of evaporation of substances like nitrogen, hydrogen, helium, etc., which become liquid at very low temperatures the above principle has been utilized by Dana and Onnes[4], Simon and Lange[5].

Simon and Lange's Apparatus.—We proceed to describe the experiments of Simon and Lange for determining the latent heat of liquid hydrogen. Their apparatus is indicated in Fig. 15. The copper calorimeter K is connected by means of German silver tubes N, R through the stop-cocks H, V to the manometer M and the hydrogen reservoirs B,B. The calorimeter K is itself suspended in a copper vessel G, the latter in turn being contained in a Dewar flask D containing liquid hydrogen. The space in G and in the Dewar flask above the liquid can be evacuated. First the pressure above the hydrogen in the Dewar flask is reduced so that it boils and its temperature falls. This causes the gaseous hydrogen to condense in the calorimeter K and then G is evacuated.

Next an electric current is passed through a heating wire W, of constantan, contained in K. Liquid hydrogen vaporizes and collects in the reservoir B. Knowing the volume of B, the rise in pressure indicated by M and the equation of state of hydrogen, the mass of liquid evaporated can be found. In addition if the electrical energy spent is known, the latent heat can be easily calculated.

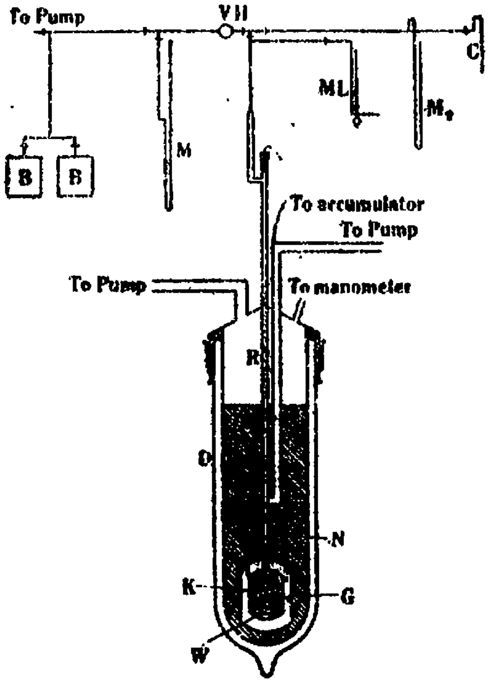

Fig. 15.—Apparatus for determining the Latent Heat of liquid hydrogen.

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[1] *Ann. d. Physik*, **29**, 44, 1909. [2] *Phys. Rev.* **33**, 181, 1911.

[3] *Journ. Amer. Chem. Soc.*, **45**, 2080, 1923.

[4] *Leiden Commun.*, No. 179c. [5] *Zeits. f. Physik*, **15**, 312, 1932.

The pressure during boiling should remain constant; this is adjusted by withdrawing V so that the reading indicated by M_2 remains constant. The temperature of boiling can be found from the vapour pressure indicated by the MacLeod gauge ML and mercury manometer M_2. The heat lost through the vacuum in G and the German silver tube is very small and can be corrected for by measuring the rate of evaporation when the supply of energy is cut off.

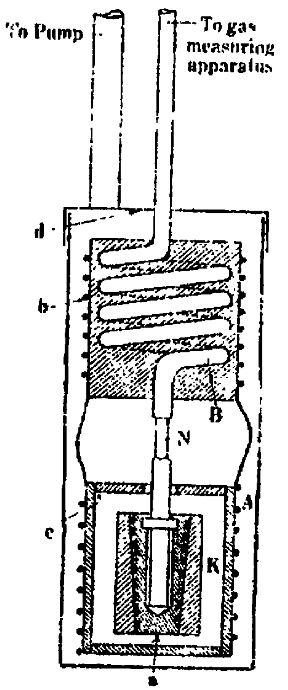

Fig. 16.—Eucken and Donath's apparatus.

11·14. Heat of Sublimation.—Eucken and Donath[1] designed an apparatus for estimating the heat of condensation and determining therefrom the heat of sublimation of solids at extremely low pressures over a large range of temperatures. Their apparatus is shown in Fig. 16.

The calorimeter consists of a copper block K, of approximately 30 calories heat capacity which is surrounded by an electrically heated adiabatic mantle A. The air between A and K is completely exhausted. The whole apparatus is now placed within a copper vessel Cu which is placed in different temperature baths. The temperature of the calorimeter is obtained by measuring the resistance of a platinum spiral embedded in the flat windings of a cone inside K (shown as finely shaded). Within this cone is also placed a heating spiral of manganin the object being to determine the heat capacity of the calorimeter by adding a measured amount of electrical energy and measuring the increase in temperature from the change in resistance of the platinum spiral. Over this manganin spiral an outer cone is exactly fitted after the lead to the windings is taken out. The vapour passes through the forecooler, the spiral B, into the calorimeter to which it is connected by the German silver tube N. B is embedded in a block of lead which is kept 2° or 3° above the temperature of the calorimeter by means of the heating spirals. A number of thermoelements are placed at a, b, c, d, for temperature regulation. The apparatus is connected to a gasometer (not shown in the diagram) from which a measured amount of gas can be led into the calorimeter and condensed. The changes of temperature in the calorimeter are continuously followed, and the total change $\triangle T$ after the condensation has taken place is determined. Neglecting radiation loss, the latent heat L is given by the relation

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[1] *Zeits. f. Phys. Chem.*, **124**, 181, 1926.

$$Ln = c\triangle T, \quad \dots \quad (15)$$

where n denotes the number of grams condensed, and c the heat capacity of the calorimeter and its contents.

With this apparatus Eucken determined the heat of sublimation of NH_3, CO_2, N_2O, HCl within the vapour pressure range 2—80 mm. of mercury.

DETERMINATION OF VAPOUR DENSITY

11·15. By vapour density we mean the specific gravity of the vapour referred to air or hydrogen as unity. The vapour density can be easily found if we determine the volume occupied by a known weight of vapour at a certain pressure and temperature. Thus if w grams of the vapour occupy v c.c. at the pressure p and temperature T and ρ_0 be the weight of 1 c.c. of the standard substance (air) at 273° and 760 mm., then the vapour density is given by

$$\frac{w}{\rho_0 v} \cdot \frac{T}{273} \cdot \frac{760}{p} \cdot \quad \dots \quad (16)$$

The density of the *unsaturated* vapour can be easily and accurately found by any one of the standard methods[1], *viz.*, of Victor Meyer, Dumas, Hofmann and others. But before 1860 there was no method for directly determining the density of *saturated* vapours. The methods adopted were all indirect in which the density of the unsaturated vapour was first determined and assuming the perfect gas laws to hold up to the saturated state, the density of the saturated vapour was determined. This assumption is however not quite justifiable, hence these methods can never give accurately the density of saturated vapour. Still however they are frequently used specially that of Victor Meyer, which is consequently described below.

Victor Meyer's method is of considerable practical importance. The apparatus (Fig. 17) consists of a cylindrical bulb B with a long narrow stem, near the top of which there is a side-tube. The lower part of the tube is surrounded by a suitable temperature bath which is kept replenished by a suitable liquid boiling at some pressure in A. Air inside the tube gets heated and is expelled at the top; after a time however a steady state is attained when no more air escapes. The substance whose vapour density is to be determined is enclosed in a thin-walled stoppered bottle and placed at *a* inside the tube. By manipulating *s* it is allowed to drop gently in B. The bottle breaks, the liquid vaporizes and thereby displaces an equal volume of air which escapes at the side-tube and is collected in the tube *t*. Knowing the mass of this air, the density of the vapour of the substance is obtained by dividing the mass of the liquid taken by the mass of displaced air.

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[1] Full details of these methods will be found in any text-book on Physical Chemistry.

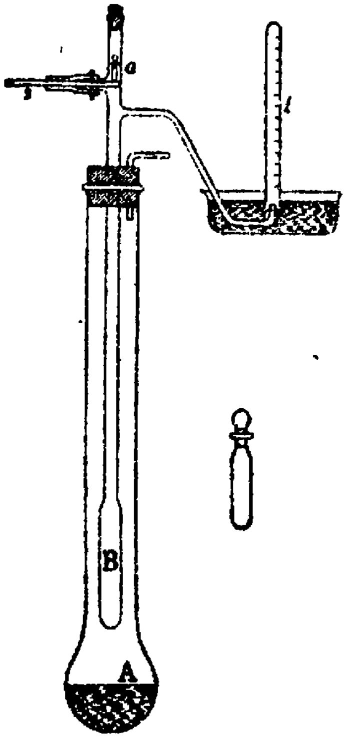

Fig. 17.—Victor Meyer's Vapour Density apparatus.

Nernst[1] modified the apparatus and could thereby measure the vapour density of KCl and NaCl up to 2000°C. while Wartenberg[2] found the vapour density of several metals up to 2000°C. For description see Arndt, *Physikalisch-chemische Technik*, Chap. IX.

11·16. Accurate Determination of the Density of Saturated Vapour.—In 1860 Fairbairn and Tate[3] devised an apparatus by means of which they measured the density of saturated vapour directly. Fig. 18 explains the principle of their apparatus. A is a spherical glass bulb whose narrow stem dips into mercury contained in the outer wider glass tube. The latter communicates with the metal reservoir B. Both A and B contain some water above the mercury levels, the latter containing a larger quantity than the former. All air is expelled from the apparatus and then both the vessels are surrounded by a bath whose temperature is gradually raised. The levels of the mercury in the two vessels remain constant, that in A being always higher than in B due to the excess of water in B. This is so as long as there is any liquid water in A. But as soon as the liquid in A disappears, the level of mercury in A suddenly rises. This is so because the saturated vapour pressure increases much faster than the pressure of unsaturated vapour obeying Boyle's law. The temperature at which this sudden rise of mercury column in A appears is noted. At this temperature the vessel A becomes filled with saturated vapour whose pressure may be found by means of a gauge connected to B. Knowing the mass of water in A and the volume of the enclosed space, the density of the vapour at the particular temperature and pressure can be calculated.

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[1] *Zeits. f. Electrochemie*, **9**, 622, 1903.

[2] *Zeits. f. anorg. Chemie*, **56**, 320, 1908.

[3] *Phil. Trans.*, **150**, 185, 1860; *Phil. Mag.*, **21**, 230, 1861.

Somewhat later Perot[1] attempted to isolate a portion of the saturated vapour and to weigh it. This could be very conveniently done by isolating by means of a stop-cock and getting the vapour absorbed in dry calcium chloride and weighing the latter. K. Onnes[2] employed another simple method. In a graduated vacuous tube different masses of the liquid were introduced. and the volumes of the vapour and the liquid observed. Thus if m and m' grams of the substance are introduced and the volume of the gas and the liquid are v_1 and v_2 in the first case, and v_1', v_2' in the second case, and ρ_g, ρ_l represent the densities of the gas and the liquid, we have

$$m = v_1\,\rho_g + v_2\,\rho_l,\quad m' = v_1'\cdot\rho_g + v_2'\cdot\rho_l.$$

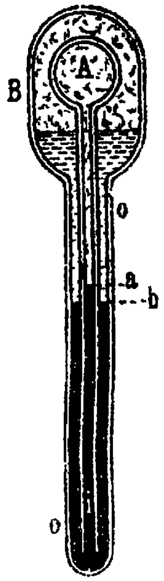

Fig. 18—Fairbairn and Tate's apparatus.

11·17. Thermodynamical Treatment of Variation of Latent Heat.

—For any change of state we have

$$\frac{L}{T} = s_2 - s_1\,, \qquad (17)$$

where L is the latent heat at temperature T, and s_1, s_2 the specific entropies of the first and the second states respectively.

For fixing our ideas we may take the subscript 1 to refer to the liquid state and 2 to refer to the vapour state. Differentiating with respect to T we get

$$\frac{dL}{dT} - \frac{L}{T} = T\left(\frac{ds_2}{dT} - \frac{ds_1}{dT}\right). \qquad (18)$$

Now $$T\,\frac{ds_1}{dT} = c_{s_1},\quad T\,\frac{ds_2}{dT} = c_{s_2}$$

where c_{s_1}, c_{s_2} denote the specific heats in the two phases. It must be however noted that c_{s_1}, c_{s_2} are neither the specific heat at constant volume nor the specific heat at constant pressure.

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[1] *Comptes Rendus*, **102**, 1369, 1886.

[2] *Leiden Commun.*, No. **117**, 1911.

Here the vapour always remains in equilibrium with the liquid and hence must always be saturated. Clausius called c_{s_2} the specific heat of saturated vapour. The pressure and volume are to be so varied that the condition of saturation continues to hold. The above relation[1] therefore becomes

$$\frac{dL}{dT}=\frac{L}{T}+c_{s_2}-c_{s_1} \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Values of c_{s_2} and c_{s_1}.—We have

$$\left(\frac{ds}{dT}\right)_{\text{sat}}=\left(\frac{\partial s}{\partial T}\right)_p+\left(\frac{\partial s}{\partial p}\right)_T\left(\frac{dp}{dT}\right)_{\text{sat}} \quad . \quad . \quad (20)$$

where the suffix "sat" denotes that the condition of saturation is satisfied. Multiplying by T, and using equations (6) and (7) of Chap. VII, we have

$$c_s=c_p-T\left(\frac{dv}{dT}\right)_p\frac{L}{T(v_2-v_1)}$$

We have $v_1=1$ c.c., $v_2=1674$ c.c. hence v_1 may be neglected. For the liquid state $dv_1/dT=\cdot 001$, and is extremely small. Hence $c_{s_1}=c_{p_1}$=specific heat of liquid water at constant pressure at 100°C.

For the gaseous state, however, dv_2/dT is large, viz., 4·813. Using these values, we have

$$c_{s_2}=c_{p_2}-\frac{4\cdot 813}{1674}\times 537=0\cdot 47-1\cdot 54=-1\cdot 07.$$

Thus the specific heat of saturated water vapour at 100°C. *comes out to be a negative quantity.* This is rather a paradoxical result but at the same time perfectly true. In Chapter II we have seen that the specific heat may vary from $+\infty$ to $-\infty$ depending entirely upon the external conditions. In the present case the condition of saturation has to be always satisfied. Now saturated water vapour has a pressure of 760 mm. at 100°C. and 787·6 mm. at 101°C., *i.e.*, the specific volume of saturated water vapour decreases as the temperature rises. This is so with all vapours. Hence when saturated water vapour at 100°C. is heated to 101°C. at constant pressure, it becomes unsaturated, and to satisfy the condition of saturation it must be compressed till the pressure becomes 787·6 mm. This compression generates heat, and in the case of water at 100°C., the heat generated is so great that some of it must be withdrawn in order that the temperature may not rise above 101°C. The net result in this case is that heat must be withdrawn from and not added to the system during the complete operation. Thus we explain physically why the specific heat of saturated vapour sometimes becomes negative.

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[1] This relation may also be deduced by the use of a cycle represented on the entropy-temperature diagram (see Fig. 3, p. 355).

From these considerations it will be seen that saturated steam must become superheated by adiabatic compression, *e.g.*, water vapour at 100°C and 760 mm. pressure, when compressed suddenly to 787 mm. would be heated by 2·1°C., and hence become superheated; conversely when the vapour at 101°C., is allowed to expand adiabatically, say from 787 mm. to 760 mm., the temperature would fall by 2·1°C., *i.e.*, to 98·9°C., and hence it would become supercooled, and partial condensation may occur. For certain vapours however the work done in compressing the substance is not so great and the specific heat of saturated vapour is positive. These become superheated by adiabatic expansion.

These conclusions were experimentally verified by Hirn in 1862. He allowed steam from boilers at a pressure of five atmospheres to enter a long cylinder fitted with glass plates at its ends. When the cylinder had attained the temperature of the steam, the supply and the exit tubes were closed, and the vapour, when viewed from the ends, looked quite transparent. The exit tube was next suddenly opened and the vapour expanded adiabatically when a dense cloud was observed inside the cylinder, thereby confirming the results from theory. Cazin employed an improved form of the apparatus and experimented with various vapours. The results agreed with theory.

For the variation of latent heat we have from (19) and (20)

$$\frac{dL}{dT} = \frac{L}{T} + c_{p_2} - c_{p_1} - T\left(\frac{dp}{dT}\right)_{\text{sat}}\left[\left(\frac{\partial v_2}{\partial T}\right)_p - \left(\frac{\partial v_1}{\partial T}\right)_p\right]. \quad . \qquad (21)$$

Now since $\left(\frac{dp}{dT}\right)_{\text{sat}} = \frac{L}{T(v_2 - v_1)}$, we have

$$\frac{dL}{dT} = \frac{L}{T} + (c_{p_2} - c_{p_1}) - \frac{L}{(v_2 - v_1)}\left[\left(\frac{\partial v_2}{\partial T}\right)_p - \left(\frac{\partial v_1}{\partial T}\right)_p\right]. \quad . \qquad (22)$$

The equation is also applicable to the case of melting of solids. It may be employed to calculate either the variation of latent heat with temperature or the specific heat at constant pressure, provided the other quantities are known.

For example let us find the variation of latent heat of fusion of ice with temperature with the help of the following data :—

$c_{p_2}=1$ (specific heat of water at 0°C.) $c_{p_1}=0 \cdot 505$ (specific heat of ice at 0°C.), $L=80$; $v_\circ=1$; $v_1=1 \cdot 09$;

$$\left(\frac{\partial v_2}{\partial T}\right)_p = -0{\cdot}00006\,; \quad \left(\frac{\partial v_1}{\partial T}\right)_p = 0{\cdot}00011.$$

Therefore $$\frac{dL}{dT} = 0{\cdot}64.$$

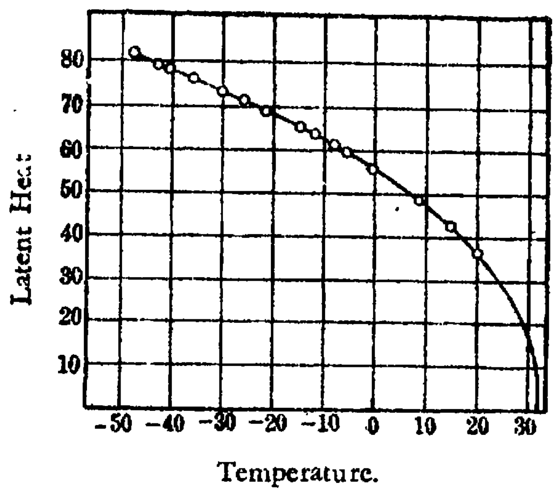

Fig. 19.—Variation of Latent Heat of CO_2 with temperature.

i.e., if by suitably adjusting the external pressure ice melts at − 1°C. the latent heat will be found to be 0·64 cal. less than the latent heat at 0°C.

11·18. Variation of Latent Heat of Vaporization.—

Experiments show that the latent heat of vaporization of a liquid diminishes continuously with temperature, and vanishes at the critical temperature (vide Fig. 19 for CO_2).

Some attempts have been made to find out whether the quantity ML/T_b, where M=molecular weight and T_b, the boiling point, shows any regularity. Table 4 illustrates such an attempt.

On the basis of the data in Table 4 Trouton enunciated his rule which states that *the ratio of the molar latent heat of vaporization to the boiling point is a constant for all substances.* The rule does not apply to substances whose vapours are associated and is further

Table 4.—*Illustration of Trouton's Rule.*

Substance	Molar latent heat in calories ML	Boiling point T_b	Value of ML/T_b experimentally
Helium	22	4·29	5·1
Hydrogen	219	20·4	10·8
Nitrogen	1340	77·3	17·3
Oxygen	1630	90·1	18·1
Hydrochloric acid	3890	188·1	20·7
Chlorine	4600	239·5	19·2
Pentane	6100	309·0	19·75
Carbon disulphide	6490	319·2	21·0
Benzene	7350	353	20·8
Aniline	10000	457·0	21·9
Mercury	14200	630·0	22·6
Caesium	15600	858	18·2
Rubidium	18700	942	19·9
Sodium	23300	1155	20·2
Zinc	27730	1180	23·5
Lead	46000	1887	24·4

only approximately true. Attempts[1] have been made to express the Trouton constant as a function of the temperature but no theoretical significance can be attached to the results in view of the fact that the boiling point is much dependent on the pressure.

Purely empirical attempts have also been made to express L as a function of T. For water, Henning expressed the results of his experiments by the formula:

$$L = 538{\cdot}06 + 0{\cdot}5996(100 - t). \qquad (23)$$

Thiessen found that for many substances, the formula $L = L_1(t_c - t)^{\frac{1}{3}}$ gives good results.

11·19. Variation of Latent Heat of Fusion.—A better empirical formula is available for the transition solid→liquid, for the melting point is not so much dependent on pressure, and the external latent heat can now be neglected. This is illustrated in Table[2] 5. The measurements on the rare gases were carried out by Clusius and his co-workers.[3]

Table 5.—*Illustration of Trouton's Rule*

Substance	Melting point T_m in °K	Molar latent heat ML in joule/g. mol.	$\frac{ML}{T_m}$	Crystal system
Na	370·7	2550	6·91	Body-centred cube
K	336·1	2300	6·74	
Rb	312	2180	6·99	
Cu	1356	11,300	8·33	Face-centred cube
Ag	1235	11,300	9·17	
Zn	692·5	7500	10·9	Hexagonal close-packed
Cd	594·0	6300	10·6	
Tl	563	6150	10·9	
Hg	234·1	2340	10·0	Hexagonal Face-centred cube
Ne	24·5	335	13·7	
A	83·8	1120	13·4	
Kr	116	1630	14·1	
H_2	13·95	117	8·4	
D_2	18·65	197	10·5	

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[1] V. Wartenberg, *Z. f. Elektrochem.*, **20**, 444, 1914; Kendall, *Jour. Amer. Chem. Soc.*, **36**, 1620, 1914; Wagner, *Z. f. Elektrochem.*, **31**, 308, 1925.

[2] Compiled from Moelwyn-Hughes, *Physical Chemistry*, p. 300 (C.U.P. 1947).

[3] Clusius and Riccoboni, *Zeits. f. phys. Chem.*, **38**, 81, 1938.

11·20. Latent Heat curve near the critical point.—Near the critical point it is difficult to determine the p-T curve, and find out the value of dp/dT. We see from eqn. (6) Chap. VII that $dp/dT=0/0$, as both L and the difference v_2-v_1 vanish. Extrapolation curves show that $dp/dT\rightarrow\infty$, but this is not definitely established.

DISCUSSION OF VAPOUR PRESSURE RESULTS

11·21. Theoretical Formula for Saturated Vapour Pressure.—Many attempts, both empirical and theoretical, have been made to obtain a mathematical expression for p as a function of T, but without complete success.

It is best to start with the equation (29) of §8·15, *viz.*,

$$\frac{dp}{dT}=\frac{L}{T(v_2-v_1)}. \qquad (24)$$

Neglecting v_1, the specific volume of the condensed phase in comparison with that of the vapour phase, we have

$$\frac{dp}{dT}=\frac{L}{Tv_2}=\frac{ML}{RT^2}p, \qquad (25)$$

assuming that the saturated vapour obeys the law of perfect gases. We have on integrating

$$\ln p=\frac{M}{R}\int\frac{L\,dT}{T^2}+i. \qquad (26)$$

Unfortunately, L does not vary with T in a simple manner (vide eqn. 22), hence the integration has to be done only in approximate stages. If L is taken to be a constant, we get a formula given by Young (1820):

$$\ln p=-\frac{ML}{RT}+i=A+\frac{B}{T}. \qquad (27)$$

If L is put equal to $L_0-\alpha T$, which roughly represents the variation of L for many substances, (26) yields

$$\ln p=-\frac{ML_0}{RT}-\frac{M\alpha}{R}\ln T+i=A+B\ln T+\frac{C}{T}, \qquad (28)$$

a formula originally given by Kirchhoff (1858), and still used for small ranges.

After a period of stagnation the S. V. P. of substances became the subject of many lively discussions owing to its importance in the study of technical gas reactions. The best approach to the problem is from eqn. (24) of Chap. VIII which states that when two phases of the same substance are in equilibrium their thermodynamical potentials have the same value in both phases.

Instead of using the Gibbs' thermodynamical potential $G=U+pV-TS$ we may use the equivalent function Ψ which is given by the relation $\Psi=-\frac{G}{T}=S-\frac{U+pV}{T}$. We have for equilibrium

$$\Psi_{\text{cond.}}=\Psi_{\text{gas.}} \qquad (29)$$

Let us now find out these quantities separately. We have for the condensed state

$$S=\int_0^T \frac{\partial S}{\partial T}\,dT+\int \frac{\partial S}{\partial p}\,dp+S_0\,, \qquad (30)$$

where S_0 is the value of entropy of the condensed phase at absolute zero (A. N.). Hence

$$S=\int_0^T C_p\,\frac{dT}{T}+S_0\,, \qquad (31)$$

neglecting $\int_0^T \frac{\partial S}{\partial p}dp=-\int_0^T V\alpha\,dp$, as α is generally very small for condensed phases. Further

$$d\,(U+pV)=C_p\,dT+V dp.$$

Hence
$$U+pV=\int_0^T C_p\,dT+\int_0^T V dp+(U+pV)_0$$

$$=\int_0^T C_p\,dT+U_0\,; \qquad (32)$$

where U_0 is the energy of the condensed phase at the A. N. The other quantities can be neglected. Hence, we have

$$\Psi_{\text{cond.}}=-\frac{U_0}{T}+\int_0^T \frac{C_p}{T}\,dT-\frac{1}{T}\int_0^T C_p\,dT+S_0$$

$$=-\frac{U_0}{T}+\int_0^T \frac{dT}{T^2}\int_0^T C_p\,dT+S_0, \qquad (33)$$

all quantities referring to the condensed phase.

To calculate Ψ for the vapour phase, we have

$$U + pV = U_0 + \int_0^T C_p \, dT,$$

as given by (32) for the condensed phase. The quantities now refer to the vapour phase. The value of C_p depends upon the constitution of the molecules composing the vapour. This cannot be taken up generally, before we take up the subject of specific heat of gases (Chap. XVI). For monatomic gases, however, we have $C_p = \frac{5}{2}\mathrm{R}$.

The value of S for vapours has been discussed in §9·11 and cannot be taken up here (vide infra, Chap. XVII) for the general case of any gas. But for monatomic gases, we have from (41) p. 391

$$\frac{S}{\mathrm{R}} = ln \frac{V}{Ng}(2\pi mkT)^{3/2} + \frac{5}{2} + \frac{S_0}{\mathrm{R}}. \quad . \quad . \quad . \quad (34)$$

where S_0 is the value of the entropy at the A. N. for the gas. Anticipating quantum theory, we put g in (34) equal to h^3, where h is Planck's constant (Chap. XV). We have then, using $pV = \mathrm{R}T$,

$$\frac{S}{\mathrm{R}} = \frac{5}{2}\, ln\, T - ln\, p + ln \frac{(2\pi m)^{3/2} k^{5/2} e^{5/2}}{h^3} + \frac{S_0}{\mathrm{R}}. \quad (35)$$

Hence Ψ/R for a monatomic gas is given by

$$\frac{\Psi}{\mathrm{R}} = -\frac{U_0}{\mathrm{R}T} + \frac{5}{2}\, ln\, T - ln\, p + ln \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} + \frac{S_0}{\mathrm{R}} \quad . \quad (36)$$

where U_0, S_0 now refer to the vapour phase.

Equating (33) and (36) we have

$$ln\, p = -\frac{\lambda_0}{\mathrm{R}T} + \frac{5}{2}\, ln\, T - \frac{1}{\mathrm{R}}\int_0^T \frac{dT}{T^2}\int_0^T (C_p)_{\text{cond}}\, dT$$

$$+ ln \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} + \frac{\Sigma S_0}{\mathrm{R}} \quad . \quad . \quad . \quad (37)$$

Here $\lambda_0 = (U_{\text{gas}} - U_{\text{cond}})_0$ = latent heat of vaporization at the A. N. and ΣS_0 stands for $(S_{\text{gas}} - S_{\text{cond}})_0$.

N.B.—The early workers assumed that the entropy of a condensed phase is 0 at the A.N. This, as will be shown subsequently, is true only when the atoms concerned can be regarded as spheres, having the same properties in all directions. But this assumption can no longer be justified, in view of the recent progress in the knowledge of the structure of atoms. Both the nucleus and the outer shells of electrons which compose the atom, may possess finite angular and magnetic moment, and are therefore generally spherically asymmetrical.

As regards the nuclei, their effect on ΣS_0 is nil, as they are the same in the solid and vapour states. As regards the electron-shell, the asymmetry may be, and is in general, different in the two phases. Only in a few cases (vide Table 6, p. 478 and discussion there) we can neglect the last term.

Now expressing λ_0 and C_p in calories, and p in atmospheres, we have the practical formula

$$\log p = -\frac{\lambda_0}{2\cdot30RT} + \frac{(C_p)_{\text{gas}}}{R}\log T - \frac{1}{2\cdot30R}\int_0^T \frac{dT}{T^2}\int_0^T (C_p)_{\text{cond.}}\, dT$$

$$+ \log\left[\frac{(2\pi m)^{3/2}\, k^{5/2}}{h^3}\right] - 6\cdot0057 + \frac{\Sigma S_0}{2\cdot3R} \quad . \quad . \quad (38)$$

The term 6·0057 is log $(1\cdot013\times10^6)$ which is the value of one atmosphere in dynes. We have further $k=1\cdot34\times10^{-16}$, $m=Mm_{\text{H}}$ (M=atomic weight, m_{H} = weight of the H-atom), $h=6\cdot54\times10^{-27}$ Using these values we get the final expression

$$\log p = -\frac{\lambda_0}{4\cdot573T} + \frac{5}{2}\log T - \frac{1}{4\cdot573}\int_0^T \frac{dT}{T^2}\int_0^T (C_p)_{\text{cond.}} dT$$

$$-1\cdot5885 + \tfrac{3}{2}\log M, \quad . \quad . \quad . \quad . \quad (39)$$

provided we put $\Sigma S_0 = 0$.

Nernst was the first to insist on the importance of the integration constant in the vapour-pressure equation. It was called by him '*The Chemical Constant*'. We have just now seen that for a monatomic substance the chemical constant C is given by

$$C = -1\cdot5885 + \tfrac{3}{2}\log M, \quad . \quad . \quad . \quad . \quad (40)$$

where M = atomic weight.

11·22. Experimental Verification of the Vapour-Pressure Formula.—The expression (39) for the vapour pressure of a monatomic substance has been subjected to a large number of experimental tests by a number of workers.

In Table 6, we have collected the available data for verifying (39). The equation shows that we require measurements of the specific heat of the solid phase up to the A.N. In many cases, the value of C_p is available up to 14°K or still lower, and in the case of Ne up to 6°K. For the lower region, the value of C_p is often extrapolated. This process is not quite satisfactory, as the value of C_p is sometimes found to vary in an unexpected way, *e.g.*, the specific heat of metals is found suddenly to increase at the superconducting stage, and that of He and many other non-metals shows a sharp and sudden rise within a very small temperature range.

Table 6.—*Chemical constant of monatomic substances*

Element	λ_0 in Kilocalories	C_0	C_e	$C_0 - C_e$	Ref.
He	0·012	—0·687 ± 0·01	—0·685	—0·002 ± ·01	1
Ne	0·516	0·367 ± 0·01	0·369	—0·002 ± ·01	2
A	1·887	0·792 ± 0·04	0·815	—0·023 ± ·04	3
Kr	2·643	1·294 ± 0·02	1·295	—0·001 ± ·02	4
Na	25·46	0·774 ± 0·1	0·455	0.319 ± ·10	5
K	21·5	1·22 ± 0·04	0·81	0·41 ± ·04	6
Cu	77·5	1·00 ± 0·40	1·11	—0·11 ± ·40	5
Ag	72·3	2·40 ± 0·40	1·45	0·95 ± ·40	5
Au	92·2	2·41 ± 0·65	1·85	0·56 ± ·65	5
Mg.	34·9	0·47 ± 0·21	0·49	—0·02 ± ·21	7
Zn	31·2	1·21 ± 0·015	1·14	0·07 ± ·15	7
Cd	27·1	1·57 ± 0·13	1·49	0·08 ± ·13	8
Hg	14·2	1·95 ± 0·06	1·86	0·09 ± ·06	3
Pb	48·3	2·27 ± 0·36	1·38	0·39 ± ·36	9
Tl	43·4	2·37 ± 0·28	2·18	0·19 ± ·28	7

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From the above table it appears that the best agreement is obtained in the case of Zn, Cd, Hg, Ne and A. In the case of other substances like Na, K, there is considerable discrepancy. For further discussion see Chap. XVII.

11·23. Vapour Pressure Formula from Kinetic considerations.—Consider a liquid in contact with its vapour and contained in an enclosure kept at a constant temperature T. We can apply Maxwell's law to the molecules in the liquid. If the liquid surface is flat, the work required to transfer one molecule from the liquid to the vapour above is λ/N, where λ is the latent heat per gram-molecule of the liquid and N is the number of molecules in a gram molecule. Hence considering the equilibrium of the liquid and vapour we have from Maxwell-Boltzmann's law[1]

$$n_g = n_l\, e^{-\lambda/NkT}. \qquad (41)$$

where n_g and n_l denote the molecular density in the vapour and the liquid states respectively. But the vapour pressure p is given by

$$p = n_g\, kT.$$

Hence

$$p = n_l kTe^{-\lambda/NkT}. \qquad (42)$$

It is difficult to investigate[2] the dependence of n_l on T, but it is easy to see that the two will be inter-dependent. Further λ also depends on T. Assuming n_l to be constant, and subject to these limitations, we deduce

$$\log p = -\frac{\lambda}{RT} + \log T + \text{const.} \qquad (43)$$

11·24. Vapour Pressure over Curved Surfaces.— The foregoing conclusions hold only when the evaporating surface is flat. When the surface is curved as in a small spherical drop of radius r, the S. V. P. is much different as was first shown by Lord Kelvin in 1870. When some water evaporates, the surface diminishes and this is accompanied by a decrease in the total surface energy of the drop. We have, mass of the drop $= (4/3)\pi r^3 \rho$.

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[1] More accurately, we should equate the number of molecules emitted by the surface per second to that absorbed by it. For detailed discussion see Müller-Pouillet, *Lehrbuch der Physik*, **3**, part 2, pp. 229—233.

[2] For detailed investigation see Bradford, *Phil. Mag.*, **48**, 936, 1942 and connected papers.

$\therefore$ The mass evaporated $= dm = 4\pi r^2 . dr . \rho$.

The diminution in surface area $dA = 8\pi r dr = (2/r\rho)\, dm$.

Diminution in surface-energy

$$= \mathscr{T} . dA = (2\mathscr{T}/r\rho) dm. \quad . \quad . \quad . \quad . \quad . \qquad (44)$$

If r is sufficiently small, this may be comparable to the latent heat, e.g., for water at 30°C, $L = 580$ cal./gm, and we have

$$L/(2\mathscr{T}/r\rho) = 580 \times 4 \cdot 2 \times 10^7 \Big/ \frac{2 \times 73}{r} = 16 \cdot 7 \times 10^7\, r.$$

Hence if $r \cong 10^{-7}$ cm., the contribution from surface energy becomes comparable to L.

When the mass dm disappears by evaporation, we have to add to each molecule the energy

$$\{\lambda - (2\mathscr{T}/r\rho)M\}/N \quad . \quad . \quad . \quad . \qquad (45)$$

because $2\mathscr{T}/r\rho$ is the decrease in surface energy per unit mass, hence $(2\mathscr{T}/r\rho)M/N$ is the decrease per molecule.

If p_r now denotes S. V. P. over the drop we have from (42)

$$p_r = n_l k T \, exp. \left[-\left(\lambda - \frac{2\mathscr{T}}{r\rho} M\right) \Big/ NkT \right] = p_\infty \, exp \left(\frac{2\mathscr{T} M}{r\rho NkT} \right), \qquad (46)$$

p_∞ denoting vapour pressure over surface of infinite radius, i.e., over flat surface. It is the same quantity as ordinary S. V. P.

This relation is of very great importance for the understanding of the formation of drops which compose a cloud. It has been long believed that when water evaporates from the sea and land under the effect of the sun's rays, air saturated with water vapour being lighter ascends in the atmosphere and in doing so, its temperature falls by adiabatic expansion. Therefore, the air becomes supersaturated, i.e., contains more vapour than it can hold and the excess is condensed in the form of drops forming a cloud or fog.

The extensive laboratory experiments of Aitken between 1880 and 1890 showed that the matter was not so simple. What he did was to allow air within a closed vessel standing over a pool of water (and therefore saturated with water vapour) to expand suddenly to a larger volume. He found as expected that a mist was formed consisting of minute water droplets which settle down within a short time. But what surprised Aitken was that if this expansion and settling of clouds was carried out a number of times, then afterwards no cloud would be formed even when the expansion was sufficient to produce a sufficiently low temperature for condensation.

This was traced to the fact that minute particles of dust which are always present in air and are considered usually as nuisance, are actually indispensable for the formation of drops. When the expansion takes place, the droplets form round the dust particles which are carried downwards when the drops settle, and when all the dust that is present in the air is removed as a result of successive settling, no further drops can be formed by adiabatic expansion. In fact, if the air in the closed space is in the very beginning freed from dust particles by passing it through fine glass-wool, no drops are formed even at the first expansion.

An explanation of this fact is easily available from formula (46). According to this we get the following ratio of p_r/p for particles of different radii as shown in table 7.

Table 7.—Values of p_r/p for drops of water.

r (cm.)	2×10^{-8}	6×10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}
p_r/p	316·2	6·91	3·16	1·127	1·012	1·001

Thus if a drop of radius 10^{-6} cm. is to be stable, the vapour above it must be supersaturated to the extent of 1·127. If this supersaturation is not available, the drop will evaporate. Let us see how these results explain Aitken's observations. A water molecule has a radius of 2×10^{-8} cm. and nearly a hundred of them must come together if a drop of radius 10^{-7} cm. is to be formed. When adiabatic expansion takes place, a number of water molecules may come together forming a drop of 10^{-7} cm. radius but this cannot be stable unless the supersaturation is 3·16. Failing this the drop evaporates as soon as it is formed. But when a dust particle of radius $r=10^{-6}$ cm. is present, water molecules depositing around it form a drop of radius 10^{-6} cm. and little supersaturation is required to make the drop stable.

Aitken's experiments and the foregoing theoretical discussion show that cloud droplets cannot be formed under the conditions of our atmosphere unless some kind of condensation nuclei are present. In addition to dust particles, other condensation nuclei which are present in air are particles of smoke, minute particles of salt which are suspended in air as a result of evaporation of salty spray carried by air currents from over the sea surface, and probably also the sulphurous fumes from industrial towns which readily get oxidised, minute nitrous oxide particles which are formed as a result of reaction of nitrogen and oxygen under ultraviolet sunlight, and charged ions present in atmosphere on account of the ionising action of ultraviolet sunlight.

It is not yet known which kind of nuclei play the predominant role in the formation of water drops constituting fogs and stratus clouds. But statistical observations show that the radii of these droplets are of the order of 20μ, *i.e.*, 2×10^{-3} cm.

The actual rain-drops which reach the ground are however of larger size; observations have shown that they range in size from a radius of 100μ (10^{-2} cm.) for light drizzle to drops of radius $2\cdot5\times10^{-1}$ cm. (largest rain-drops). This can be quite easily explained, for when a droplet of radius r is suspended in air, though subjected to free gravity, it falls with a steady velocity due to the viscous drag of air. The limiting velocity for small drops is, according to Stokes' law, given by $2gr^2/9\eta$ where r=radius of the drop, η=coefficient of viscosity. The velocity varies as r^2, and calculation shows, that a droplet of 10μ radius will take 20 hours to fall 1 km. By that time, it will evaporate. A drop of 3×10^{-2} cm. radius falls one km. in 6 min., and the time is too short for evaporation.

Though droplets of water occurring in clouds have probably all sizes ranging from 10^{-7} cm. to $2\cdot5\times10^{-1}$ cm., meteorologists draw an artificial line at $r=100\mu$. Particles of smaller radius than this are called cloud droplets, and particles of larger radius are called rain-drops. Most non-rain-bearing clouds like fog and low-lying stratus, are composed of cloud droplets. They evaporate without giving rain.

This brings out the question how rain-drops are formed in our atmosphere, for evidence shows that when water-vapour condenses round nuclei, their sizes are of the order of 10^{-3} cm. radius. Such drops do not reach the ground. There is some other agency which makes such droplets grow bigger to the size of rain-drops as compose rain-bearing clouds like nimbo-cumulus.

When the temperature is sufficiently low, below the ice-point, the water vapour should condense directly into ice particles, but observations show that this does not usually happen. Cloud chamber experiments have shown that in the absence of dust no fog is formed unless T is $<-41\cdot2$°C. At lower temperatures, a mixture of water drops and ice-particles is formed, the proportion of the latter increasing with cooling. When some dust particles are present, this temperature may be as low as −32°C, but water condenses more as liquid drop than ice-particles.

This is in accordance with observations made in aeroplane ascents which show that even when the top of a cloud is below the freezing level, the cloud mostly consists of liquid drops. Such drops are 'Supercooled', i.e., they convert into ice-particles when they strike against an aeroplane side. In fact, the phenomenon of supercooling is so frequent that Langmuir thinks it is wrong to say that water freezes to ice below 0°C. A more correct description would be that once formed, ice cannot exist above 0°C.

Supercooled water-drops have a considerably different vapour pressure than ice-particles at the same temperature as is clear from table 8.

Table 8.—*Saturated Vapour Pressure of Water and Ice.*

Temperature in °C	0	−10°	−20°	−30°	−40°	−60°
Over water in mb.	6·11	2·87	1·26	·527	·189	·020
Over ice in mb.	6·11	2·62	1·04	·284	·129	·011

This shows that when ice particles and water drops exist side by side, as in high-level clouds, the atmosphere there may be undersaturated with respect to water, but supersaturated with respect to ice. This will promote the evaporation of water drops and the growth of ice-particles at their expense.

According to Bergeron, this phenomenon, also known as the '*Ice-crystal effect*', is mainly responsible for the conversion of cloud particles to rain-drops. When the top of a cloud reaches somewhat above the freezing level, the ice-particles grow at the expense of liquid drops, and in course of time, become heavy enough to fall quickly and on reaching the lower levels, melt into rain-drops. In fact, according to Bergeron, 'rain' is only melted snow.

These ideas form the basis of the methods of artificial rain-making. Clouds may often appear and disappear without producing rain. Even when the tops of such clouds extend higher up than the freezing level it may consist of merely supercooled water-drops. What the rain makers do, is to 'seed' the tops of such clouds with powdered dry ice (solid CO_2), which brings down the temperature at places below and produces a few ice crystals. Once they are formed, they begin to grow according to the Bergeron process, and the cloud may be precipitated as rain. Another method proposed, and reported to be carried out successfully is to sprinkle tops of clouds with powdered crystals of AgI. Ice-particles grow round the dust of AgI and then the Bergeron process takes place.[1]

PROBLEMS

1. Show that the latent heat of vaporisation of a van der Waals gas is given by the relation $\lambda = -a\left(\frac{1}{V_g} - \frac{1}{V_l}\right) + p\,(V_g - V_l)$ and hence show that the latent heats of two gases at corresponding temperatures are in the ratio of their a/b.

2. Use eqn. (40) to calculate the chemical constant of the electron.

3. Deduce the vapour pressure formula for a polyatomic gas assuming that for the vapour $C_p = \frac{5}{2}R + C_i$.

4. Vapour pressure of barium is $5{\cdot}34 \times 10^{-6}$ mm. at 798°K and $6{\cdot}74 \times 10^{-3}$ mm. at 973°K. Calculate its latent heat of sublimation at the absolute zero.

BOOKS RECOMMENDED

1. Müller-Pouillets—*Lehrbuch der Physik*, Vol. 3, part II, pp. 459-481.

2. Glazebrook—A *Dictionary of Applied Physics*, Vol. 1, article on 'Latent Heat'.

3. *Handbuch der Experimental-physik*, Vol. 8, Part 1, pp. 527-598.

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[1] For fuller details see articles in *Science and Culture* by A. K. Ray and K. R. Saha, Nov. 1948.

CHAPTER XII

PRODUCTION OF LOW TEMPERATURES

12·1. Introduction.—In the early days of the study of heat the melting point of ice was chosen as the zero (starting point) of the scale of temperatures. This was done more for the sake of convenience than from a desire to start the temperature scale from the lowest temperature attainable. The study of the laws of perfect gases tells us that we can, at least theoretically, proceed on the Celsius scale 273 degrees below the melting point of ice and that this is the lowest temperature conceivable. This idea of absolute zero first deduced from the gas scale was set on a firmer ground by thermodynamical reasoning (Chap. VI). This point (–273·16°C.) is therefore taken as the zero of the absolute temperature scale. In our ordinary experience we have not to deal with temperatures much below 0°C., but in this chapter we shall describe the principles and contrivances by which bodies can be continuously deprived of heat, and the region from 0°C to absolute zero can be reached.

The following methods may be employed to produce refrigeration :—

(i) By adding a salt to ice.
(ii) By boiling a liquid under reduced pressure.
(iii) By the adiabatic expansion of a gas doing external work.
(iv) By utilizing the cooling due to Joule-Thomson effect.
(v) By utilizing the heat of adsorption. (Desorption method).
(vi) By utilizing the cooling due to Peltier effect. This cooling is rather small though semi-conductor thermo-junctions have recently produced much more cooling.
(vii) By the process of adiabatic demagnetisation. This is useful only in the region of liquid helium temperatures and has been utilized to produce the lowest temperatures.

(*i*) BY ADDING A SALT TO ICE.

12·2. Freezing Mixtures.—Low temperatures may be attained by adding a salt or acid to water or ice, as was done by Fahrenheit. The cause of this lowering of temperature is easily understood. Pieces of ice have generally some water adhering to them, and if salt be added to this ice, it is dissolved by the water and more ice melts. The necessary heat for this process, *viz.*, the heat of solution and the latent heat required to melt the ice, is extracted from the mixture itself whose temperature consequently falls down. This is the principle of *freezing mixtures* which are simply solutions or mixtures of this type. This process however cannot go on indefinitely. For every salt there is a corresponding eutectic temperature (see p. 369), below which the temperature cannot be lowered in this way. If more salt be added, it no longer goes into solution and hence no further cooling can be produced.

Table 1. *Freezing Mixtures.*

Salt	Anhydrous salt per 100 grams of mixture	Eutectic Temperature
$MgSO_4$	19·0	—3·9°C
$ZnSO_4$	27·2	—6·5
KCl	19·7	—11·1
NH_4Cl	18·6	—15·8
NH_4NO_3	41·2	—17·4
$NaNO_3$	37	—18·5
NaCl	22·4	—21·2
$MgCl_2$	21·6	—33·6
$CaCl_2$	29·8	—55
$FeCl_3$	33·1	—55
$ZnCl_2$	51·0	—62
KOH	31·5	—65

In Table 1 the composition of the eutectic mixture and the corresponding eutectic or cryohydric temperatures are given for a number of commoner salts. The amount of anhydrous salt, which is contained per 100 grams of the eutectic mixture, is given in the table. Generally hydrated salts are employed and in that case the corresponding quantity of the hydrated salt should be obtained by calculation. These eutectic temperatures represent the lowest temperature that is possible to attain with the particular freezing mixture.

This method of refrigeration by adding salt to ice is employed in the common ice-cream freezers. A solution containing milk and sugar is kept in a vessel which is surrounded by a mixture of ice and common salt. The vessel is then rotated rapidly for the thorough mixing of ice and salt and after some time the solution begins to freeze which is indicated by the increasing difficulty felt in the process of rotation. After this has continued for some time the ice-cream is ready. A mechanical arrangement for quick and efficient mixing is given in *Journ. Amer. Chem. Soc.*, Vol. 54, p. 3886 (1932) by R. C. Archibald.

(*ii*) By the rapid evaporation of a liquid.

12·3. Cooling by Evaporation.—Low temperature may be produced by the rapid evaporation of a liquid, which requires heat for its conversion to the gaseous state; e.g., if one gram of water at 100°C. is evaporated from a certain volume, 537 calories are needed, and if this volume is isolated, this heat will be taken from the volume of water, which will consequently fall in temperature.

The amount of cooling which can be produced depends on the nature of the liquid and the rate of evaporation, besides other factors. The rate of evaporation can be accelerated by using pumps of high suction capacity, as in vapour compression machines (vide infra §12·4) or by promoting evaporation by absorbing the vapour in another liquid or by other methods. The cryophorus described in elementary text-books, is a machine in which evaporation of water in one limb of the closed U-tube is promoted by immersing the other limb in ice.

This principle is used widely in pure laboratory research for the production of low temperature, e.g., it was used by Kamerlingh Onnes for pushing the low temperature limit by allowing liquefied helium (temp. 4·2°K) to boil at low pressure by continuously removing the vapour by a suction pump. In this way, when the pressure was reduced to 0·013 mm. by suction the temperature fell to 0·82°K.

For practical purposes, the process has to be made quick and continuous. This is done in the vapour compression and vapour -absorption machines by special contrivances described below.

12·4. Vapour-compression Machines.—The machine (Fig. 1) consists of three principal parts:

(1) A compressor G, usually electrically driven, which is fed by gas boiling under low pressure from an evaporator E through an intake valve.

(2) The gas is compressed adiabatically and delivered to the condenser · Q, which is generally a coil of copper embedded in a vessel through which some coolant (cold water

or brine water) is passing. Sometimes the coils are also cooled by fan-driven air currents. The heat of compression is carried off by the coolant, and the vapour becomes liquefied.

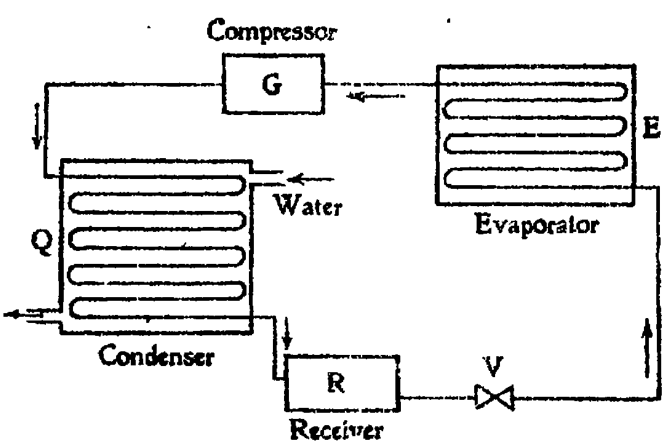

Fig. 1.—Vapour Compression Machine.

(3) The liquid refrigerant now passes to the reservoir R, from which through an expansion valve V, it is delivered to the evaporator, and another cycle starts.

The evaporator coils are embedded in the refrigerator system. This may be fan-driven air in air-conditioning apparatus, a refrigerator chest, or any other system.

Any liquid can be used as a refrigerant—water, ammonia, SO_2, CO_2, freon, etc., but in practice the choice is limited to a few. The criteria for selection of the proper liquid are :—(1) It should have a large latent heat of evaporation; (2) The vapour should have a small specific volume; (3) It should have sufficient vapour pressure at the temperature of the evaporator (about 5°F) so that atmospheric air may not be sucked in through any possible leakage. Further it should easily liquefy when compressed and cooled in the condenser (temp. about 86°F); (4) It should have desirable chemical properties, i.e., should be non-inflammable and non-toxic, should not be explosive and should have no chemical action on the machinery.

Table 2 gives the liquids which are generally used together with a comparison of their properties.

12·5. Refrigerators based on Vapour-absorption.—Evaporation of a liquid may also be promoted by quick absorption of its vapour in another liquid, e.g., by the absorption of ammonia vapour in water. This was the basis of a continuous form of freezing machine due to Carré which was formerly employed on a large scale. The working of the machine will be understood from Fig. 2. The generator A contains a strong solution of ammonia gas in water and is heated by a burner. Ammonia gas is expelled from the solution and passes into the coils immersed in the condenser B through which cold water continuously flows. The gas condenses there under its own pressure (from

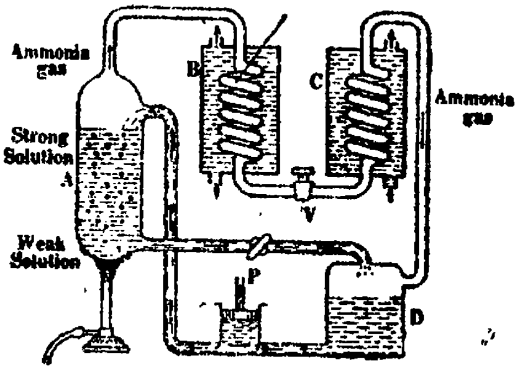

Fig. 2.—Ammonia Absorption Machine.

Table 2.—Characteristics of Refrigerants.[1]

Item	Ammonia	Sulphur dioxide	Carbon dioxide	Methyl chloride	Freon-12 CCl_2F_2
1. Boiling point in °C at atmos. pressure.	−33·35	−10·1	−78·6	−24·09	−29·8
2. Latent heat of evaporation at 5°F in calories per gram.	313·8	97·5	63·7	99·2	38·6
3. Refrigerating effect in calories per gram	268·9	78·81	31·47	78·20	28·34
4. Vapour pressure at —15°C in atm./cm.^{2}	2·33	·803	22·7	1·42	1·80
5. Vapour pressure at 30°C in atm./cm.^{2}	11·52	4·52	70·7	6·50	7·34
6. Specific volume of vapour in evaporator in c.c. per gm.	508·9	400·6	16·66	282·8	92·7
7. Power in kw. for a refrigerating effect[2] of 50·4 K. cal./min.	0·726	0·742	1·37	0·751	0·744
8. Coefficient of performance.	4·85	4·74	2·56	4·67	4·72

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[1] For properties of other refrigerants see *Refrigerating Data Book* (1943-1944) published by American Society of Refrigerating Engineers, New York.

[2] This capacity is also called one ton of refrigeration per 24 hr., or simply "ton" of refrigeration. For the method of calculating the various quantities in this table see §12·8.

5 to 12 atm.) into liquid ammonia. The liquid ammonia thus formed passes through a narrow regulating valve V to the spiral immersed in the refrigerator C, where on account of the low pressure it evaporates. The valve is adjusted to maintain the desired difference of pressure on the two sides. Water placed round the refrigerating coils C is thereby cooled sufficiently to be frozen to ice.

The ammonia gas formed in the coils in C is absorbed by water or dilute ammonia solution contained in the absorber D and thus the pressure is kept low (about 2 atm.). The solution in D becomes concentrated and, is transferred by the pump P to the generator at the top. The heat evolved in absorption is removed by cooling water. Thus the supply of concentrated ammonia solution is kept up. Dilute ammonia from the bottom of the generator may be run to the absorber and concentrated. The cycle is thus repeated and the action is quite continuous.

The difficulties of the machine are that it has a low efficiency, and the pressures are widely different in the condenser and evaporator. Besides it has a moving part in the pump needed to transfer the liquid to the generator. All these difficulties are avoided in a clever invention by two Swedish engineers, von Platen and Munters[1], which is placed in the market under the name Electrolux Refrigerator. In this Dalton's law of partial pressures is used to make the total pressures in the condenser and the evaporator equal, maintaining at the same time a difference in partial pressures of ammonia in the two chambers; this is accomplished by using an inert gas like hydrogen. The principle of the machine can be easily grasped from Fig. 3. b is a vertical steel cylinder containing ammonia solution and c is a tube projecting inside the cylinder which can be heated electrically, or by a flame. d is a rectifier, e a water-cooled tube (condenser) where the vapour is compressed to a liquid, f is the evaporator, g the partition blades, h the absorber and i, a jacket for circulation of cold water.

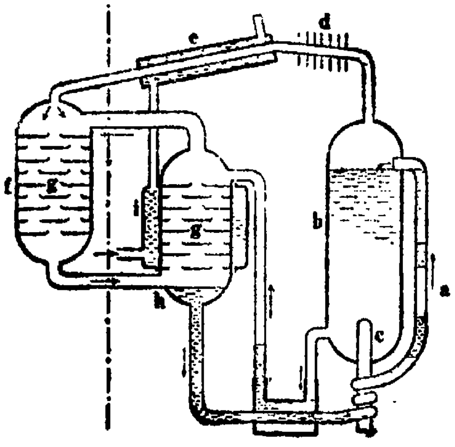

Fig. 3.—The Electrolux.

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[1] *Die Naturwissenschaften*, **4**, 651, 1926.

The vapour as it rises from b passes through d, where the water vapour carried by ammonia is condensed and flows back to b. The ammonia vapour is condensed at e, and flows by the action of gravity to f. This vessel can withstand a pressure of 12 atmospheres and has circulating through it hydrogen gas in such quantity that the partial pressure of ammonia is 3 atmos. and that of hydrogen is 9 atmos. As liquid ammonia enters f, it evaporates on account of its low partial pressure and mixes with hydrogen; this is still more facilitated by the partition blades. The mixture is heavier than pure hydrogen, so it sinks down and is absorbed at the bottom of h, from where it passes back to b owing to the action of gravity and pressure produced by heating c. The hydrogen which is not absorbed passes up the partition blades in h and is again borne down by the main stream from e. Thus hydrogen is confined to the evaporator and the absorber and is prevented by liquid seals from entering the condenser or the generator, which contain pure ammonia or ammonia solution at a pressure of 12 atmos. On account of the slow velocity of circulation the total pressure throughout the system is the same, the motive power coming wholly from the heat applied to c. Due to this continuous circulation of evaporating ammonia f is cooled and a block of ice grows round it. Owing to the heating, concentrated ammonia solution is forced up a into b while weak ammonia solution is transferred from b to h.

(*iii*) ADIABATIC EXPANSION OF COMPRESSED GASES.

12·6. Cooling produced by the sudden Adiabatic Expansion of compressed gases.—If a highly compressed gas be suddenly allowed to expand adiabatically, it cools very considerably on account of the large external work it does on expanding, vide §2·28, p. 83 where it is shown that $T'=T(p'/p)^{(\gamma-1)/\gamma}$. Thus if CO_2 confined in a cylinder at 150 atm. is suddenly released to atmospheric pressure, $T' = 300\,(1/150)^{\cdot 3/1\cdot 3}=96°K$. The temperature is so low, that the issuing matter solidifies and can be caught in a piece of cloth as solid CO_2 (dry ice).

Cailletet[1] first liquefied oxygen in 1877 by this method. He compressed oxygen to a pressure of 200 atmospheres in a strong capillary tube cooled to $-29°C.$ and suddenly reduced the pressure. A mist of liquid oxygen was formed which disappeared in a few seconds. Pictet compressed oxygen to a pressure of 320 atmos. and cooled it to about −110°C. by liquid carbon dioxide evaporating under reduced pressure. Then he suddenly reduced the pressure by opening a nozzle. Liquid oxygen shot out of the nozzle evaporating immediately. In 1884 Wroblewski obtained a mist of hydrogen while in 1893 Olszewski obtained liquid hydrogen in sufficient quantities, by cooling compressed hydrogen with liquid oxygen and then suddenly releasing the pressure.

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[1] *Comptes Rendus*, **85**, 1213, 1270, 1877.

The process is however essentially discontinuous and is not very useful for the continuous production of liquefied gases. Hence for commercial purposes it was almost discarded; but a novel way of utilizing the principle in combination with others was invented by Claude and Heylandt for liquefying air and by Kapitza for liquefying hydrogen and helium. Recently it has gained importance by its successful use in Collin's liquefier for liquefying helium.

We have described above two types of refrigerating machines. There is a third type also which utilizes the principle mentioned above in this section. This is called the *air-compression machine* because air is here used as the refrigerant. The working of the machine is explained in Fig. 4.

Air is first compressed adiabatically in the compressor P (Fig. 4.), the compressed gas is then passed through a water cooler C where it is cooled at constant pressure. This cool high-pressure air suffers adiabatic expansion in the expansion cylinder E of an engine to a pressure equal to the pressure of the compressor intake and becomes considerably cooled. This cold air then traverses the refrigerator or the cold storge space R and absorbs heat at constant pressure and subsequently returns to the compressor and the cycle continues. The work necessary for the compressor is partly obtained from the expansion cylinder E and partly from a separate motor M. This is the principle of the Bell-Coleman refrigerator largely used for the refrigeration of cold storage chambers in ships.

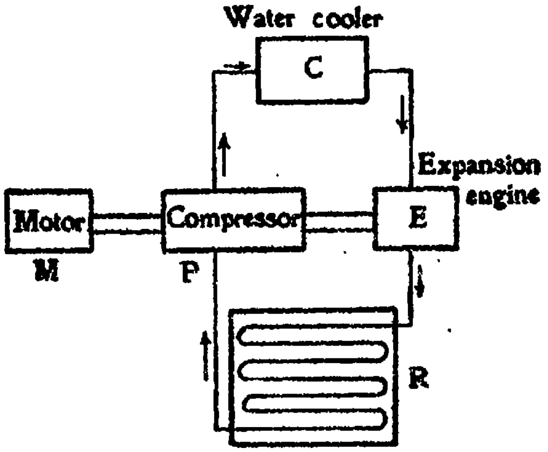

Fig. 4.—Air-expansion refrigerating machine.

PERFORMANCE OF REFRIGERATING MACHINERY.

12·7. Coefficient of Performance.—We define β, the coefficient of performance (sometimes also called 'cop') by the relation

$$\beta = \frac{\text{Amount of Heat removed}}{\text{Work done in running the machinery}}.$$

Before finding out β for the different machinery so far described and to be described later, let us find out the β of an ideal Carnot engine which, according to §4·5—4·8, can be worked *backwards* along the route ADCBA extracting the heat Q' from the heat sink T', and after performance of work W on it by a compressor, transfers $Q = W + Q'$ to the heat source T. We have therefore for the Carnot engine

$$\beta = \frac{Q'}{W} = \frac{Q'}{Q-Q'} = \frac{T'}{T-T'}, \ \beta = \frac{1-\eta}{\eta}, \quad \quad (1)$$

where η is the efficiency of the Carnot engine.

It is easy to see, by following the same arguments as given in §4·8, that no refrigerating machine can have a higher 'cop' than the Carnot engine, but its use as a refrigerator is precluded by the same considerations as given there. The machine would be too slow-acting and would require an enormous expansion ratio. Still, the Carnot engine is used as a standard of reference for comparing the 'cop' of other systems.

12·8. Vapour-compression Machines.—The working of the vapour-compression machines is similar to that of the engines using steam, only working backwards. We can use fig. 6, p. 244. The refrigerant liquid (NH_3, SO_2 or Freon) is allowed to come from the liquid receiver R (Fig. 1, p. 488) through the expansion valve V, and evaporate within the coils of the refrigerator E at pressure p, which is the S. V. P. of the liquid at the temperature at which the refrigerator is maintained (−15°C in our example), and all the time absorbing heat from the body to be cooled; this may be flowing air (for an air-conditioner), brine or water to be frozen. In Fig. 6, p. 244 this is indicated by the line DC. When the point C is reached the vapour is adiabatically compressed in the compressor along the path CB to the pressure p_2, which is the S. V. P. of the refrigerant at the temperature of the coolant water in the condenser. The heat of the compressed vapour is removed by water (temperature 30°C) keeping the pressure constant, till all the vapour has condensed to a liquid at 30°C (point A in Fig. 6). The liquid is then allowed to flow to the receiver (point D), and a fresh cycle begins.

We can apply the results of §4·10 to this case bodily. We have

$$\beta = \frac{1-\eta}{\eta} \quad \frac{H_C - H_D}{H_B - H_C} \qquad . \quad . \quad . \quad . \quad (2).$$

Let us now illustrate by means of an example, in which NH_3 is used as a refrigerant. We have $T_D = T_C = -15°C$ (temperature at which the refrigerator is maintained), $T_B = T_A = 30°C$ (temperature of coolant water or air). Then

p_C = S. V. P. of $(NH_3)_{liq}$ at $-15°C = 2{\cdot}41$ kg/cm².
p_B = „ „ „ $30°C = 11{\cdot}9$ kg/cm².

From Mollier's liq. ammonia chart,[1] we can find out that $H_C = 340{\cdot}7$, $H_B = 396{\cdot}3$, $H_D = 77{\cdot}2$ k. cal per kg of NH_3. Hence

$$\beta = \frac{H_C - H_D}{H_B - H_C} = \frac{263{\cdot}5}{55{\cdot}6} = 4{\cdot}74.$$

For Carnot ideal

$$\beta = 258/45 = 5{\cdot}73.$$

$$\therefore \text{Relative efficiency} = 4{\cdot}74/5{\cdot}73 = {\cdot}827.$$

The mass-flow rate m of refrigerant per k. cal./min. of refrigerating effect is given by

$$m = \frac{1}{H_C - H_D} = \frac{1}{263{\cdot}5} = 3{\cdot}80 \times 10^{-3} \text{ kg/mm.} \qquad . \quad (3)$$

Work W to be done for transference of heat is given by

$$W = H_B - H_C = 55{\cdot}6 \times 3{\cdot}8 \times 10^{-3} \text{ k. cal/min.} \quad . \quad . \quad (4)$$
$$= 1{\cdot}472 \times 10^{-2} \text{ KW.}$$

The required compressor capacity

$V_c = 3{\cdot}8 \times 10^{-3}$ × volume of one kg of NH_3 at p_C, T_C (condenser pressure and temperature).
$= 1{\cdot}931$ litres per min.

If we have to remove 252 k. cal per min. which is nearly 5 tons of refrigeration, the power required would be 3·7 KW, and the displacement nearly 486·6 litres per min.

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[1] See Perry, *Chemical Engineers' Handbook*, McGraw-Hill Book Co, (1941).

N.B. The refrigeration engineers in the U.S.A. and England generally use the Fahrenheit scale and British Units. One British Thermal Unit (B.T.U.) is the quantity of heat required to raise 1 lb. of water through 1°F. Hence

$$1 \text{ B.T.U.} = 453{\cdot}6 \times \frac{5}{9} = 252 \text{ cal.} = {\cdot}252 \text{ k. cal.}$$

The unit of refrigeration is known as the 'Ton of Refrigeration' which means removal of $2{\cdot}88 \times 10^5$ B.T.U. per day of 24 hours or 200 B.T.U./min. It is based upon the consideration that to melt 1 ton of ice would require the extraction of $2{\cdot}88 \times 10^5$ B.T.U. 1 Ton of Refrigeration is thus equal to the removal of $5{\cdot}04 \times 10^5$ cal. or 50·4 k. cal. per min.

12·9. The 'Cop' of Gas-expansion-Engines.—These engines have been described in §12·6, Fig. 4. Since the heats are taken in and rejected by the working substance at constant pressure the working of the machine can be explained by referring to Fig. 13, p. 257, the cycle AFCD being taken backwards. The gas which enters the compressor at the point F (pressure p_1, generally atmospheric temperature T_f), is compressed adiabatically to p_2, T_a (point A). The compressed gas is cooled at this pressure to the temperature T_d of the coolant, usually water, (point D), and is then allowed to expand adiabatically in the expansion cylinder to the point C (p_1, T_c). The cold gas is now led through the refrigerator R from which it absorbs heat at constant pressure along CF, the gas reaching the state F and the cycle is completed.

We have now, assuming that a gm-molecule of the gas is in use,

$$Q = \text{heat given to coolant} = C_p\,(T_a - T_d).$$

$$Q' = \text{heat abstracted from refrigerator} = C_p(T_f - T_c).$$

Now, as proved on p. 258,

$$(p_2/p_1)^{(\gamma-1)/\gamma} = \frac{T_d}{T_c} = \frac{T_a}{T_f} = \frac{T_a - T_d}{T_f - T_c}. \qquad (5)$$

The work done,

$$W = Q - Q' = C_p\,\{(T_a - T_d) - (T_f - T_c)\}. \qquad (6)$$

Hence
$$\beta = \frac{Q'}{W} = \frac{1}{(p_2/p_1)^{(\gamma-1)/\gamma} - 1}. \qquad (7)$$

We shall illustrate it by an example. Let $T_f = -15$°C, and suppose we have found by calculation that to maintain the space to be cooled at this temperature, we have to absorb heat at the rate of $2{\cdot}40 \times 10^5$

cal, or 240 k. cal./min. Cooling water is available at 30°C. Let us suppose that the ratio p_2/p_1 is 5. Then we have since $(5)^{(\gamma-1)/\gamma}=1\cdot584$,

$$\beta = \frac{1}{1\cdot584-1} = 1\cdot71.$$

$$T_f = 258, \quad T_d = 303,$$

from which we calculate

$$T_a = 2581 \times \cdot584 = 408\cdot7, \quad T_e = \frac{303}{1\cdot584} = 191\cdot3.$$

Weight of air to be circulated:

$$= \frac{2\cdot40\times10^5}{\cdot24\ (T_f-T_e)} \text{gm./min.} = \frac{2\cdot40\times10^5}{\cdot24\times66\cdot7} \text{ gm./min.}$$

$$= 14\cdot99 \text{ kg./min.} = 33\cdot06 \text{ lb./min.}$$

The power needed to drive the engine is given by

$$W = \frac{Q'}{\beta} = \frac{2\cdot40\times10^5 \text{ cal/min.}}{1\cdot71} = 140 \text{ k.cal/min.} = 9\cdot8 \text{ KW.}$$

$$\left(1 \text{ KW} = \frac{10^{10}}{4\cdot2\times10^7} = 238 \text{ cal./sec.}\right)$$

Such a machine would be regarded as inefficient. The 'cop' of the corresponding Carnot engine is $T_f/(T_d-T_f) = 258/45 = 5\cdot73$.

Exercise 1. Calculate the minimum amount of work necessary to convert 50 gm. of water at 0°C and 1 atmos. pressure into ice at the same temperature and pressure, using a reservoir at 30°C.

2. What is the least amount of work, expressed in kilowatt-hours, necessary to convert 50 gm. of water from 30°C to ice at −10°C using a reservoir of cooling water at 30°C., assuming that c_p of ice = 0·5 cal./gm. deg. C. and the pressure is kept constant.

3. A vapour compression ammonia machine is used to maintain a space at −15°C and the temperature of the cooling water available is 30°C. If the machine absorbs 10 tons of refrigeration, calculate the power required, the coefficient of performance and the compressor displacement. (Use ammonia tables).

LIQUEFACTION OF GASES.

12·10. Liquefaction by application of pressure and low temperature.—Just about the beginning of the nineteenth century the number of liquids which could be used for production of low temperature by rapid evaporation was extremely limited. Though it was felt that many substances which occur as gases at ordinary temperatures, would become liquid if subjected to sufficiently low temperatures, and still lower temperatures could be produced by rapid evaporation of these liquids, the principles for liquefying gaseous substances were not clearly understood. It was vaguely felt that compression of gases would bring the molecules closer, and reduction of temperature would reduce their energy and the combined effect of compression and cooling would ultimately lead to the liquefaction of all gases.

Faraday (1823) was the earliest to try this effect of combined cooling and compression, and his experiment of heating substances yielding chlorine in one limb of a stout closed bent U-tube, and immersing the other limb in an ice chamber and thus getting chlorine as a yellow liquid, is a classical example of this method. Thilorier in 1835 was successful in liquefying CO_2 by the use of a similar apparatus.

By applying this process Faraday and others succeeded in liquefying a large number of gases but some, viz., oxygen, nitrogen, hydrogen, etc., baffled all attempts at liquefaction, though sometimes enormous pressures up to 3000 atmos. were used. They were therefore termed *permanent* gases.

The cause of these failures became apparent with Andrews' discovery of the critical temperature in 1863. This subject has already been treated in Chap. X. Andrews' experiments first established clearly that for every substance, which usually occurs in the gaseous form, there exists a temperature above which it cannot be liquefied however high may be the pressure to which it is subjected. Hence in order to liquefy a gas by this method it must be pre-cooled below its critical temperature.

12·11.—The principal methods of liquefying air and other gases are the following :—(1) Pictet's cascade method which utilises a series of liquids with successively lower boiling points but the principle is the same as explained above in §12·10; (2) the Linde and Hampson's methods employing the Joule-Thomson effect; (3) the Claude and Heylandt methods which utilise the cooling produced when a gas expands doing external work, and further cooling is produced by Joule-Thomson expansion. We shall now consider these methods in greater detail. Of these the first is historically the oldest and theoretically the most efficient but is somewhat cumbersome and is very little used at present.

12·12. The Principle of Cascades or Series Refrigeration.—This method was first employed by R. Pictet[1] in 1878. In principle it may be described as a number of compression machines in series. Pictet employed machines containing sulphur dioxide or carbon dioxide and nitrous oxide for the liquefaction of air. Kamerlingh Onnes[2] later employed the combination of methyl chloride and ethylene for liquefying oxygen. The principle of the method is illustrated in Fig. 5. Machine 1 utilizes methyl chloride. This has got a critical temperature of 143°C. and hence at room temperature it can be easily liquefied by the application of a pressure of a few atmospheres only. Water at room temperature flows in the jacket in (1). Liquid CH_3Cl falls into the jacket in (2) which is connected to the suction side of the compression pump. Thus the liquid evaporates under reduced pressure and its temperature falls to about —90°C. The compressor returns compressed CH_3Cl gas through the tube inside jacket (1), which is shown straight but is really in the form of spirals.

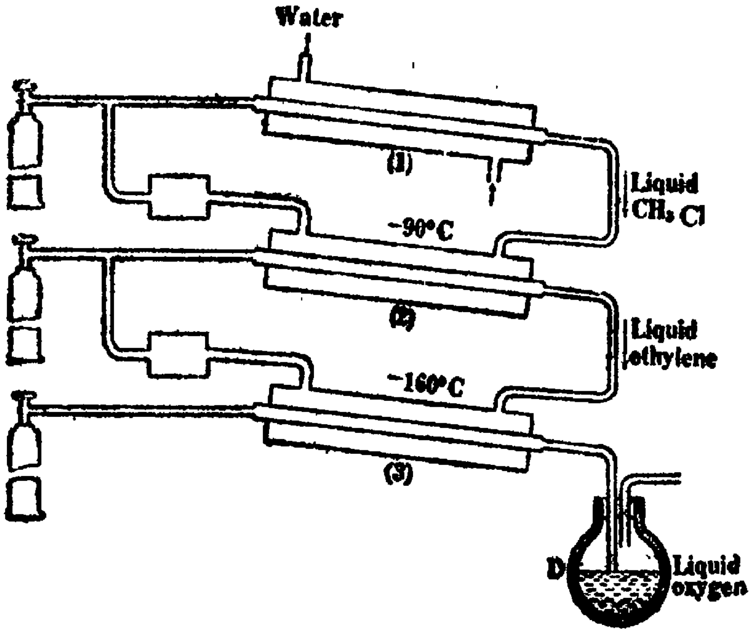

Fig. 5.—Illustration of the Method of Cascades.

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[1] *Comptes Rendus*, **85**, 1214, 1220, 1878.

[2] *Leiden Commun.*, **87**, 3, 1903; **14**, 17, 1894.

Inside the jacket (2) is placed the condenser coil through which ethylene passes from the compressor or the gas cylinder. On account of the pressure and the low temperature ethylene liquefies in jacket (2) and then enters jacket (3) as liquid. There it evaporates under reduced pressure and the temperature thus falls to about −160°C. Through the tube inside jacket (3) oxygen from a cylinder passes and liquefies under pressure. Liquid oxygen collects in the Dewar flask D. The lowest temperature obtained by allowing oxygen to boil under reduced pressure is −218°C. which is much higher than the critical temperatures of neon, hydrogen and helium, and hence the method of cascades failed to liquefy these three gases. The efficiency of the machine can be calculated in the manner explained in §12·8.

The method of cascades is very useful for laboratory purposes. The use of the compressor can be entirely dispensed with by the use of suitable liquids boiling under atmospheric or reduced pressures. The suitable liquids can be selected from table 3 which gives the normal boiling point, the critical temperature and the triple point for the common gases and will be found useful for the method of cascades. The triple point represents the lowest temperature which can be obtained by allowing the liquid to evaporate under reduced pressure, while the critical temperature represents the highest temperature at which

Table 3.—Critical temperature, normal boiling point and triple point of gases.

Gas	B. P. at 1 atmos. pressure	Critical temperature	Triple point
Methyl chloride ..	−24·09°C.	143·0°C	−102·9°C
Sulphur dioxide ..	−10·1	15·7	..
Carbon dioxide ..	−78·6	31·0	..
Nitric oxide ..	−89·8	36·50	−102·3
Ethylene	−103·72	+9·50	−169
Methane	−161·37	−82·85	−183·15
Carbon monoxide ..	−190·9	−138·7	..
Oxygen	−182·95	−118·82	−218·4
Nitrogen	−195·78	−147·13	−209·86
Neon	−245·92	−228·71	−248·67
Hydrogen ..	−252·76	−239·91	−259·14
Helium	−268·83	−267·84	..

the liquid can exist. Thus the interval between the critical temperature and the triple point represents the range in which the liquid is available. From the table we see that with the help of suitable liquid baths we can reach down to −218°C. by the method of cascades but cannot go lower than this. Still lower temperatures can be obtained by further reducing the pressure over the liquid when it solidifies. Thus using solid nitrogen and a good pump a temperature of about −224°C. can be obtained which is still above the critical temperature of neon and it is not possible[1] to bridge the gaps between nitrogen and neon, and between hydrogen and helium in this way.

12·13. Joule-Thomson Effect (Adiabatic Throttling of Gases).—Gay-lussac and Joule's experiment which proved that the internal energy U is independent of the volume of the gas, i.e., $(\partial U/\partial V)_T=0$, has been described in §2·27 (p. 81). This is true only of perfect gases. Actually a small cooling effect was found for the usual gases. This shows that U depends on the volume occupied by the gas.

To find out how the internal energy varies with the volume, Lord Kelvin in 1852, in collaboration with Joule, devised a modification of the Gay-lussac-Joule experiment, which is usually known as the porous plug experiment. In this, a highly compressed gas is being continuously forced at constant pressure through a constricted nozzle or porous plug. The plug, as its name implies, consists simply of a porous material, say cotton-wool, silk, etc., having a number of fine holes or pores and is thus equivalent to a number of narrow orifices in parallel (see Fig. 6). The gas during its passage through the pores becomes *throttled* or wire-drawn, *viz.*, the molecules of the gas are drawn further apart from one another. This is always the case whenever a fluid has to escape through a partly obstructed passage. The gas thus suffers a volume expansion. On either side of the plug constant pressures p_A, p_B are maintained, the pressure p_A on the side from which the gas flows being much greater than the pressure p_B on the other side, since the plug offers great resistance to the flow of the gas. This expansion is of a character essentially different from the Joule's expansion, where the gas expanded without doing any external work. Here it expands against a *constant* external pressure and hence has to do external work also, together with any internal work, while some work[1] is done on the gas as well. The plug is surrounded by a non-conducting jacket so that the process is adiabatic in the sense that no heat enters or leaves the system. For such processes we now proceed to show that the *total heat function* $H=U+pV$ remains constant.

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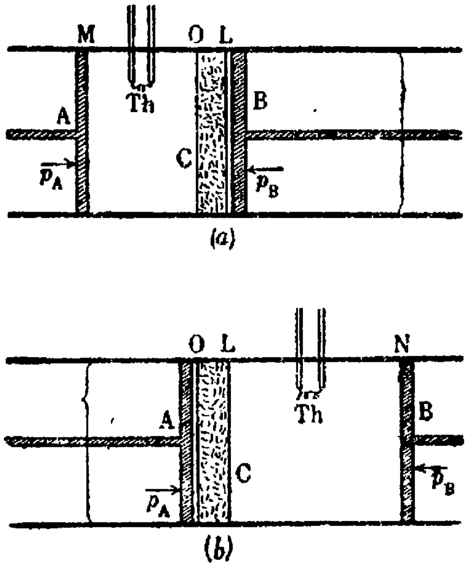
[1] Simon and others (*Physica*, **4**, 879, 1937) claim to have reached with great difficulty a temperature of about 40°K.

To prove this theorem let us consider a mass of the fluid traversing the porous plug C (Fig. 6) from left to right and assume that the steady state on both sides of the plug has been attained. Let p_A, V_A, T_A, U_A and p_B, V_B, T_B, U_B be the pressure, volume, temperature and internal energy of one mol of the fluid before and after traversing the orifice respectively. Suppose that one mol[2] of the gas is contained between the porous plug and some point M on the left and also between the plug and some point N on the right. For visualising the process we may assume imaginary piston A at M separating this quantity of the gas and that the flow of the gas is caused by the forward motion of the piston A. Actually however the rest of the gas exerts a pressure p_A at M which is maintained by the source of supply. The gas after traversing the plug pushes forward the imaginary piston B whose motion is opposed by the pressure p_B of the gas to the right of B. Thus at the beginning of the process the gas was confined in the space ML occupying the volume V_A (shown at *a*) and at the end of the process the portion of the gas which was at M has now reached O and that at L has reached N, the gas being contained in ON occupying the volume V_B (shown at *b*). Thus the mass of gas contained in MO and NL are equal but the volumes are of course unequal.



(*a*)

(*b*)

Fig. 6.—The Porous Plug Experiment.

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[1] In the process described in §12·6 this work was non-existent, and hence a large cooling was obtained there.

[2] We must consider the same mass of gas on both sides of the plug.

The gas during its passage through the orifices in the plug has to overcome friction, viscosity, etc., and loses energy. The escaping gas issues in the form of eddies and its temperature falls considerably just at the jet because some energy is now changed to the form of mass motion of the gas (this effect is spurious and is not what we want). The eddies however subside after traversing a short distance and the temperature consequently rises. Let us consider only the steady flow before and after transmission through the orifice, *i.e.*, at points far removed from the plug where eddies are not present. We assume that the gas moves very slowly so that the energy of mass motion is small and negligible in comparison to the energy of thermal motions. Our initial system is ML containing the gas MO and the plug OL; the final system is ON consisting of the gas LN and the plug OL. Since the plug is initially and finally exactly in the same state the complicated processes occurring in it do not affect our energy equation if the conditions are perfectly steady. Since the tube is surrounded by a non-conducting material, no heat enters or leaves the system. The system does not gain or lose heat by conduction at A and B since the temperature on the two sides is constant throughout the gas. Hence for this change of the system from MO to LN, $\Delta Q=0$. Some work is however done by the external forces on the slowly moving system. The force acting at A is equal to $p_A \times S$ where S is the cross-sectional area of the cylinder. The work done by this force upon the gas is $p_A \times S \times \text{MO}=p_A V_A$. Similarly the work done by the gas in forcing the piston B is $p_B V_B$. Therefore the net work done by the gas is $p_B V_B - p_A V_A$ and from the first law of thermodynamics, since $\Delta Q=0$, the work done by the system is equal to the decrease in its internal energy $U_A - U_B$, *viz.*,

$$p_B V_B - p_A V_A = U_A - U_B\,, \qquad . \quad . \quad . \quad . \quad (8)$$

or

$$U_A + p_A V_A = U_B + p_B V_B \qquad . \quad . \quad . \quad . \quad (9)$$

Hence the total heat function $H = U + pV$ remains constant in the throttling process.

Let us now calculate the change in temperature consequent on a Joule-Thomson expansion. We have

$$H=U+pV, \qquad dH=dU+pdV+Vdp=TdS+Vdp.$$

Since H does not change,

$$dH = T\left\{\left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp\right\} + Vdp = 0. \quad . \quad (10)$$

Now, $T\left(\frac{\partial S}{\partial T}\right)_p = C_p,\quad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p.$

Hence from (10), we have

$$C_p\,dT - \left(T\frac{\partial V}{\partial T} - V\right)dp = 0\ ,$$

or $$\left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right] = \frac{1}{\rho c_p}\left(\frac{T}{v}\frac{\partial v}{\partial T} - 1\right) = \mu, \quad . \quad (11)$$

where c_p, v refer to 1 gm. of the substance and ρ is its density. This gives us the differential Joule-Thomson co-efficient μ.

If however the pressure difference be large, we have from (11)

$$\triangle T = \int_{p_2}^{p_1}\frac{1}{C_p}\left(T\frac{\partial V}{\partial T} - V\right)dp = \frac{1}{C_p}\int_{p_2}^{p_1} C_p\,\mu\,dp. \quad . \quad . \quad (12)$$

C_p is the mean specific heat and p_1 and p_2 are the two pressures. ΔT gives us the Integral Joule-Thomson co-efficient.

For a perfect gas $\left(T\frac{\partial V}{\partial T} - V\right) = 0$, hence the Joule-Thomson effect vanishes. For a general discussion of its value in the case of actual gases, we take another expression for μ.

We can also write (11) in the form

$$C_p\,dT = -\left\{T\left(\frac{\partial S}{\partial p}\right)_T + V\right\}dp,$$

or $$C_p\left(\frac{dT}{\partial p}\right)_H = -\left(\frac{\partial U}{\partial p}\right)_T - \frac{\partial}{\partial p}(pV)_T\ . \quad . \quad . \quad . \quad (13)$$

The first term on the right-hand side measures deviation from Joule's law while the second gives the deviation from Boyle's law, and the Joule-Thomson effect is the resultant of deviations from both these laws.

Now $(\partial U/\partial p)_T$ is always negative, for that part of the internal energy which is due to molecular attractions always decreases with decrease of volume, i.e., increase of pressure. Hence due to deviations from Joule's law alone, the Joule-Thomson effect will be a cooling effect. Upon this will be superposed the effect of deviations from Boyle's law which is a cooling effect, if $\frac{\partial(pV)}{\partial p}$ is negative (i.e., N_2 before the bend in Fig. 6, p. 432), and a heating effect if $\partial(pV)/\partial p$ is positive (*cf.* H_2 or CO_2 after the bend).

12·14. The Porous Plug Experiment*.—The porous-plug experiment was first carried out by Joule[1] and Thomson. They employed a cylindrical plug, which is indicated in Fig. 7. The compressed gas flows through a copper spiral immersed in a thermostat and after having acquired its temperature, passes through the porous plug W. The plug consists of silk, cotton-wool or other porous material, kept in position between two pieces *ss* of wire gauze and enclosed in a cylinder of some non-conducting wood *bb*. The plug and part of the tube is surrounded by asbestos contained in a tin cylinder *zz* so that no heat reaches it from the bath. The temperature drop occurring in the process is measured by the thermocouples as indicated. Joule and Thomson worked with air, O_2, N_2, CO_2 between 4° and 100°C., the initial and final pressures being 4·5 atmospheres and 1 atmosphere respectively.

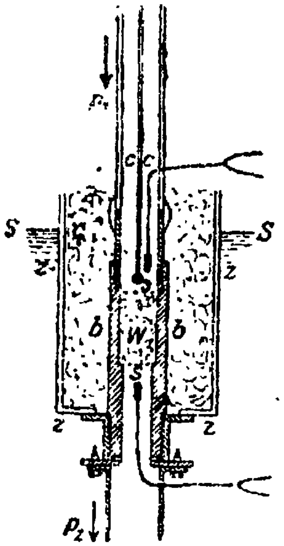

Fig. 7.—Joule-Thomson's porous plug.

Some of the subsequent workers employed plug of the "axial flow" type as used by Joule and Thomson, while some others employed a plug of the "radial flow" type. In the latter the gas flowed from the outer side of a hollow cylindrical plug to the interior and hence heat insulation was better. Certain others employed only a throttle valve or a restricted orifice. Among the recent workers may be mentioned

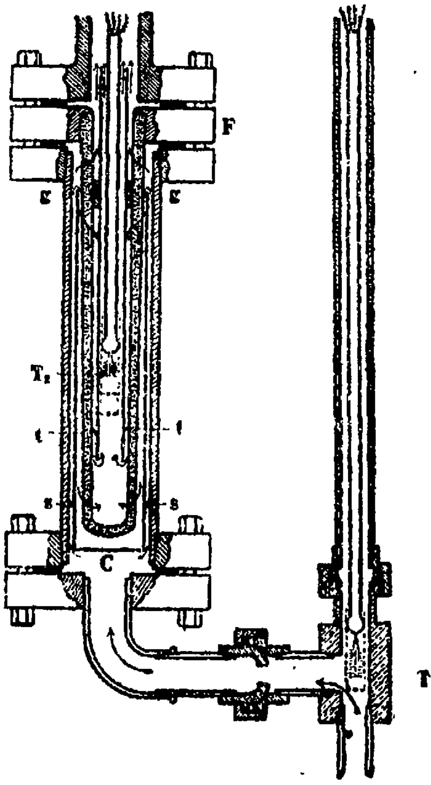

Fig. 8.—Hoxton's apparatus.

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*It is called porous-plug experiment because Lord Kelvin carried it out with porous plug, though now it ca be done in different ways.

[1] Joule *Scientific Papers*, Vol. II, p. 216.

Kester[1], Hoxton[2], Burnett[3], Roebuck[4] and Eumorfopoulos and Rai[5]. We shall describe the experimental arrangement of Hoxton who measured the Joule-Thomson effect for air at various temperatures.

The plug is shown in Fig. 8. Gas from the compressor traverses a pipe 8 metres in length kept immersed in a constant temperature bath. The pressure of the gas in the compressor is kept constant. The gas then flows past the thermometer bulb T_1, then enters the plug casing at C and travels upwards between the walls of the casing and the tinned radiation shield *ss*. Part of the gas then flows downwards, then radially into the interior of the hollow cylindrical plug which was made of earthenware. In this process the gas suffers Joule-Thomson expansion and then flows past the thermometer T_2. *gg* is a "guard ring" which prevents the conduction of heat from the support F along the material of the plug and its affecting the thermometer T_2. Inside the plug is a glass tube *tt* which makes the lower part of the gas flow past T_2. The gas escapes up the tube and is collected and compressed again. The other part of the gas passing through the plug above *gg* does not flow past the thermometer T_2. The pressure drop was measured by a differential manometer and the change in temperature by resistance thermometers. Steady conditions could be obtained only after an hour.

12·15. Experimental Results and their Discussion.—

Joule and Thomson and subsequent workers found a small cooling effect on expansion for the ordinary gases, as expected, while for hydrogen, they found to their surprise, slight heating on expansion. For a perfect gas $T\frac{\partial V}{\partial T} - V = 0$, so none of the gases was found to be perfect, while hydrogen was found to be, to use the language of Regnault, more than perfect (plus que parfait). Later helium was also found to show a heating effect.

This paradox was removed after the application of the van-der Waals' equation of state to the problem. It can be proved that

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[1] *Phys. Rev.*, **21**, 260, 1905.

[2] *Phys. Rev.*, **13**, 438, 1919.

[3] *Phys. Rev.*, **22**, 590, 1923.

[4] *Phys. Rev.*, **22**, 79, 1932; *Proc. Amer. Acad.*, **60**, 537, 1925.

[5] *Phil. Mag.*, **2**, 961, 1926.

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{2a(V-b)^2 - bV^2RT}{RTV^3 - 2a(V-b)^2}\,\frac{V}{C_p}$$

$$= \frac{1}{C_p}\,\frac{\dfrac{2a}{RT}\left(1-\dfrac{b}{V}\right)^2 - b}{1-\dfrac{2a}{RVT}\left(1-\dfrac{b}{V}\right)^2} \qquad . \quad . \quad . \quad (14)$$

$$= \frac{1}{C_p}\left[\frac{2a}{RT} - b\right] \text{ approx.} \qquad . \quad . \quad . \quad (15)$$

neglecting b/V and $2a/RTV$. Hence $\partial T/\partial p$ is positive, *i.e.*, when ∂p is negative there is cooling as long as $T < 2a/bR$.

At T greater than $2a/bR$ the gas becomes heated on suffering Joule-Thomson expansion. The temperature given by $T_i = 2a/bR$ is called the *temperature of inversion*, since on passing this temperature the Joule-Thomson effect changes its sign. It will be easily seen that $T_i = 2a/bR = (27/4)T_c$ approximately, where T_c is the critical temperature of the gas. Actually the relation does not hold, on account of the fact that van der Waals' equation does not hold accurately for any gas.

For ordinary gases T_i as Table 3 shows, is greater than the temperatures at which the JT-expansion was carried out, hence a cooling effect was obtained. For hydrogen and helium $T_i < 300$°K, hence a heating effect was found. It was subsequently found that if hydrogen and helium were sufficiently precooled, they showed cooling on JT-expansion.

If we do not neglect b/V and $2a/RTV$, which is not permissible at high pressures, we have, using (14),

$$\mu = \frac{1}{C_p}\left[\frac{2a}{RT} - b - \frac{6ab}{R^2T^2}\,p\right] \text{ approx.} \qquad . \quad . \quad . \quad (16)$$

Further for a van der Waals' gas C_p can be shown to be approximately given by (use equation 24, p. 334)

$$C_p = C_{p0} + \frac{2a}{RT^2}\,p - \frac{3ab}{R^2T^3}\,p^2.$$

Combining these two, we get the dependence of μ on p and T.

Figure 9 is taken from a paper by Roebuck and Osterberg[1] to illustrate the actual experimental results on the JT-effect of N_2. The abscissa represents the temperatures at which the JT-effect was carried out, and the ordinate the JT-cooling μ. The curves are drawn for different initial pressures. The following points may be noted:—

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[1] *Phys. Rev.*, **48**, 454, 1935.

(1) For the same temperature, μ is greater at lower initial pressures in accordance with (16).

(2) For a definite pressure, μ passes through a maximum, and decreases to zero on both sides. There are thus two inversion temperatures for JT-effect, corresponding to a definite initial pressure.

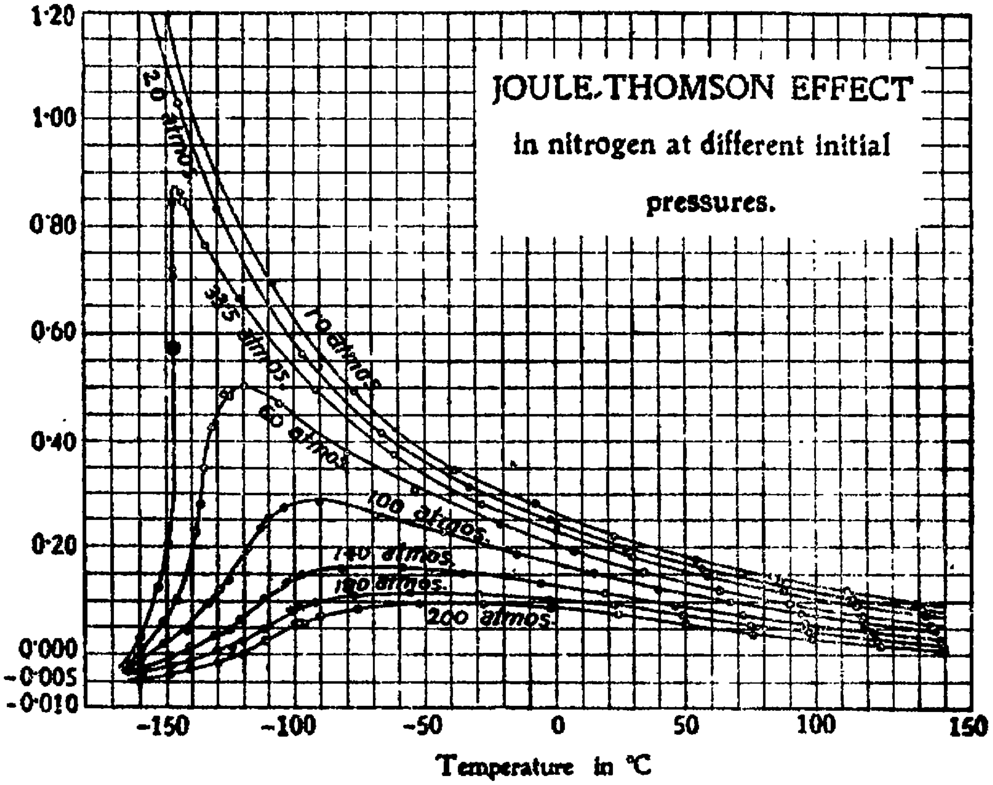

Fig. 9.—Experimental values of the Joule-Thomson effect of nitrogen.

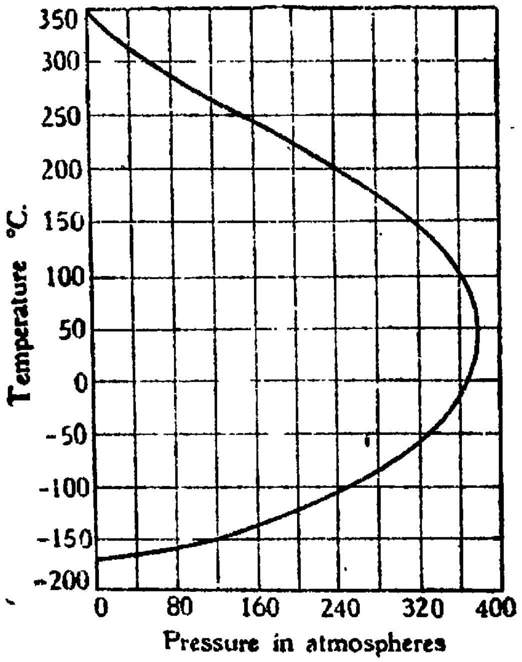

Fig. 10.—Inversion curve for N_2 obtained experimentally.

From the figure it is seen that corresponding to the initial pressure of $p=200$ atmos. there are two inversion temperatures, -120°C. and 225°C. The lower one is near T_c, the critical temperature of the gas, and the upper corresponds to $6 \cdot 75 T_c$.

These characteristics are in general explained by (16) but not quantitatively.

12·16. Curve of Inversion.

—We have seen above that the temperature of inversion depends upon the initial pressure. A curve giving the inversion temperature at different initial pressures is called the inversion curve. Fig. 10 shows such a curve for nitrogen and is obtained from the experimental data of Roebuck and Osterberg. To have a cooling effect the J.T.-expansion should be carried out at points to the left of the inversion curve.

The inversion curve is more conveniently explained by using the reduced equation of state of van der Waals' (eqn. 52, p. 429). From this we have, using the suffix r to denote the reduced scale,

$$\frac{8}{3}\left(\frac{\partial T_r}{\partial V_r}\right)_{p_r} = p_r + \frac{3}{V_r^2} - \frac{6}{V_r^3}\left(V_r - \frac{1}{3}\right). \quad . \quad . \quad (17)$$

From (11) we have for the temperature of inversion

$$\frac{T_r}{(\partial T_r/\partial V_r)_{p_r}} - V_r = 0. \quad . \quad . \quad . \quad . \quad (18)$$

Combining (17) and (18) and using the van der Waals' equation we get

$$p_r V_r^2 = 9(2V_r - 1) \quad . \quad . \quad . \quad . \quad . \quad (19)$$

for the curve of inversion. Using Amagat's coordinates $p_r V_r = y$, $p_r = x$, (19) yields

$$y^2 = 9(2y - x), \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

which is a parabola. Such a theoretical inversion curve is given in Fig. 11 and predicts quite well the general trend of the experimental curve in Fig. 10, since $p_r V_r$ can be written approximately as function of T_r.

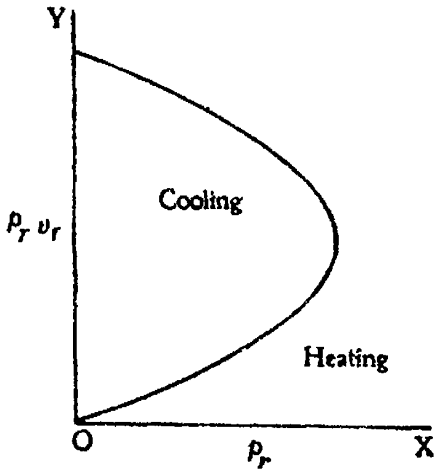

Fig. 11.—Theoretical inversion curve.

12·17. Integral Joule-Thomson Effect.—The integral Joule-Thomson effect, i.e., cooling $(T_1 - T_2)$ produced when the pressure drops from p_1 at temperature T_1 to pressure p_2, is obtained by integrating (11). We have

$$\int_{T_1}^{T_2} C_p\, dT = \int_{p_1}^{p_2} \left(T\frac{\partial V}{\partial T} - V\right) dp. \quad . \quad . \quad (21)$$

Since most equations of state are not explicit in V, we can write

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v .$$

At constant T this gives

$$\left(\frac{\partial V}{\partial T}\right)_p dp = -\left(\frac{\partial p}{\partial T}\right)_v dV. \quad . \quad . \quad . \quad (22)$$

Further $$\int Vdp=\int d(pV)-\int pdV. \quad . \quad . \quad . \quad (23)$$

Hence (21) yields

$$\overline{C}_p(T_2-T_1)=-\int_{V_1}^{V_2}T\left(\frac{\partial p}{\partial T}\right)_v dV+\int_{V_1}^{V_2}p\,dV+p_1V_1-p_2V_2 \qquad (24)$$

where $\overline{C}_p$ is the mean specific heat at the lower pressure and V_2 is the volume at pressure p_2 and initial temperature T_1.

The calculation of the right-hand side of (24) is somewhat difficult. It may be done either graphically from values of μ determined in the laboratory, or from some equation of state (say the Beattie-Bridgeman equation). Dodge (p. 302) cites an example : the cooling produced in the adiabatic throttling of air from 215 atmos. to 1·2 atmos., initial temperature 0°C, was obtained from Roebuck's experiment to be −42·8°C, while an application of the Beattie-Bridgeman equation gave −44·6°C.

There is an extensive literature and data on Joule-Thomson cooling for different gases, but they do not appear to have been analysed critically for finding out a correct equation of state for gases.

Exercise 1.—Prove that

$$dH=C_p\,dT+\left[V-T\left(\frac{\partial V}{\partial T}\right)_p\right]dp.$$

[Use the result of Problem 7, p. 336 and the relation $TdS=dH-Vdp$.]

2. Show that the heat absorbed by a van der Waals' gas during isothermal expansion is

$$\triangle Q=a\left(\frac{1}{V_1}-\frac{1}{V_2}\right)+p_2V_2-p_1V_1.$$

3. Calculate the drop in temperature produced by the adiabatic throttling expansion of air from 215 atmos. to 1·2 atmos., the air being initially at 0°C. What would be the cooling if the expansion were reversible doing useful external work ?

Assume that air obeys van der Waals' equation with $a=13{\cdot}4\times10^5$ atmos.×cm^6 per gm. mole, $b=36{\cdot}5$ c.c./gm.-mole and $\overline{C}_p=6{\cdot}95$ cal. per gm-mole, $\gamma=1{\cdot}40$. [Ans. 28·7°C ; 211°C.]

4. Calculate the temperature of inversion of air from the values of a and b given in Ex. 3.

12·18. Application of Joule-Thomson effect for Correcting the Gas Thermometer.—Equation (11) can be at once utilised for giving the absolute thermodynamic scale from observations on an ordinary gas thermometer. For we have

$$T\left(\frac{\partial V}{\partial T}\right)_p = C_p\left(\frac{\partial T}{\partial p}\right)_H + V, \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where all these quantities ought to be measured on the thermodynamic scale. If however we use a gas or any other thermometer to measure this temperature (θ), and C_p' denotes the specific heat on this arbitrary scale we have

$$C_p = \frac{dQ}{dT} = \frac{dQ}{d\theta}\cdot\frac{d\theta}{dT} = C_p'\frac{d\theta}{dT}; \quad \left(\frac{\partial T}{\partial p}\right)_H = \frac{dT}{d\theta}\left(\frac{\partial \theta}{\partial p}\right)_H .$$

$$\therefore\ C_p\left(\frac{\partial T}{\partial p}\right)_H = C_p'\left(\frac{\partial \theta}{\partial p}\right)_H .$$

Further
$$\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial V}{\partial \theta}\right)_p \frac{d\theta}{dT} .$$

Hence (25) yields

$$\int_{T_1}^{T_2}\frac{dT}{T} = \int_{\theta_1}^{\theta_2}\frac{\left(\frac{\partial V}{\partial \theta}\right)_p d\theta}{V + C_p'\left(\frac{\partial \theta}{\partial p}\right)_H} . \quad . \quad . \quad . \quad (26)$$

The quantities occurring on the right-hand side can be measured on any thermometer; all that is necessary is that the same thermometer should be used in all these measurements. Further these quantities vary with temperature, hence their dependence upon θ should be experimentally known in order that the integration can be performed. Supposing this to be done and taking θ_1 and θ_2 to refer to the melting point of ice and boiling point of water we have

$$\log_e (T_{100}/T_0) = x,$$

where x is the value of the integral within the limits 0 and 100°. Then since by definition $T_{100} - T_0 = 100$ we have

$$\log_e \frac{T_0 + 100}{T_0} = x, . \quad . \quad . \quad . \quad . \quad (27)$$

which determines T_0. Any other temperature T_1 can be found from the relation

$$\log_e \frac{T_1}{T_0} = \int_0^{\theta_1}\frac{\left(\frac{\partial V}{\partial \theta}\right)_p d\theta}{V + C_p'\left(\frac{\partial \theta}{\partial p}\right)_H} . \quad . \quad . \quad . \quad (28)$$

In general however there are not sufficient data to give accurately the variation of Joule-Thomson effect with temperature. Hence the method is not of much practical use and the other method described in-

§1·7 is generally employed for correcting the gas scale. We shall however illustrate this method by a numerical example assuming that the various quantities on the right-hand side remain constant. Then (26) yields

$$\frac{dT}{T} = \frac{dV}{V+\mu C_p'},$$

or on integrating,

$$T = a(V+\mu C_p'), \quad . \quad . \quad . \quad . \quad (29)$$

where μ stands for the Joule-Thomson effect $(\partial\theta/\partial p)_H$ and a is a constant. This shows that T is related to V in a complicated way. Then proceeding as before we have

$$\frac{T_0}{T_{100}-T_0} = \frac{T_0}{100} = \frac{V_0+\mu C_p'}{V_{100}-V_0},$$

or

$$T_0 = \frac{1}{\alpha}\left(1+\frac{\mu C_p'}{V_0}\right), \quad . \quad . \quad . \quad . \quad (30)$$

where α denotes the coefficient of expansion $(V_{100}-V_0)/100V_0$. This determines T_0 and then with the help of (29) any other temperature can be calculated.

The results for a few gases have been calculated and are given in Table 5. For hydrogen the Joule-Thomson cooling is $-0·039$°C. per atmos. $C_p = 6·86\times4·18\times10^7$ ergs per °C., $V_0 = 22·4\times10^3$ c.c. and $\alpha = 0·0036613$.

Table 5.—Joule-Thomson correction to the gas thermometer.

Gas	Volume coefficient of expansion α.	Joule-Thomson cooling per atmos.	Uncorrected temperature of melting ice $\theta_0 = 1/\alpha$	Correction term $\frac{C_p'}{\alpha V_0}\ \frac{\delta T}{\delta p}$	Thermodynamic temperature T_0
H_2	·0036613	−0·039°C	273·13	−0·13	273·0
Air	·0036706	+0·208	272·44	+0·70	273·14
CO_2	·0037100	1·005	269·4	+4·4	273·9

$$\therefore\ T_0 = 273·13\left(1-\frac{·039\times6·86\times4·18\times10^7}{10^6\times22·4\times10^3}\right)$$

$$= 273·13\ (1-·00050) = 273·0.$$

For air the data are most reliable and yield the value $T_0 = 273·14$. It will be seen that though for the various gases the melting point on the uncorrected gas thermometer ($\theta_0 = 1/\alpha$ in column 4) is much different, the melting point corrected by making use of the Joule-Thomson effect comes to about 273°C.

LIQUEFACTION OF GASES BY JOULE-THOMSON COOLING

12·19. Principle of Regenerative Cooling[1].—The Joule-Thomson cooling observed for most gases is very small. Thus for air at a temperature of 20°C when the pressures on the two sides are 50 atmospheres and 1 atmosphere respectively, Joule and Thomson found that the temperature falls by 11·7°C. Even using a pressure of 210 atmos. the fall is only 42°C. But the effect is intensified by employing what is called the *regenerative* process. A portion of the gas which first suffers Joule-Thomson expansion and becomes cooled is employed to cool other portions of the incoming gas before the latter reaches the nozzle. The incoming gas becomes still more cooled after traversing the nozzle. In this way the cooling effect can be rendered cumulative. In actual practice, this is secured by using either concentric tubes as in Linde's process or by means of Hampson spirals (§12·21). Two or more concentric tubes are arranged in the form of spirals, the inner one carrying the high-pressure inflowing gas while the outer one the low-pressure outflowing gas. In the regenerative method a further advantage is gained by the circumstance that the lower the temperature the greater is the Joule-Thomson cooling.

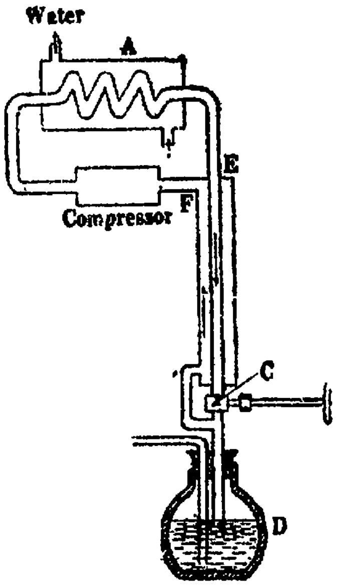

Fig. 12.—Illustration of the Regenerative Cooling.

The regenerative principle is illustrated diagrammatically in Fig. 12, where the high-pressure gas from the compressor enters the spirals contained in the water-cooled jacket A. The gas next enters the regenerator coils at E and by expansion at the valve C becomes cooled by a small amount. This returns by the outer tube abstracting heat from the high pressure gas, and reaches F almost at the same temperature as the incoming gas at E. The gas is again compressed, cooled by A and re-enters at E. As time passes, the gas approaching C becomes cooled more and more till the Joule-Thomson cooling at C is sufficient to liquefy it, *viz.*, its temperature reaches the value at which the gas would liquefy under the pressure prevailing at F. A portion of the escaping gas then condenses inside the Dewar flask D. At this stage the temperature throughout the apparatus becomes steady and may be represented by the curve shown in Fig. 13. The part LM represents the continuous decrease of temperature of the gas as we approach the nozzle through the inner tube while MN represents the Joule-Thomson cooling. NL represents the temperature of the low-pressure gas which is less than that of the adjacent high pressure gas at every point of the coil. Thus the cooler low-pressure gas abstracts heat from the incoming stream. In the ideal case, the temperature of the low-pressure gas at F should be the same as that of the high-pressure gas at the entrance E.

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[1] Pollitzer, *Zeits. f. d. ges. Kalte-Ind.*, **28**, 125, 1921; Linde, *Zeits. d. Verb. d. Ind.*, **65**, 1356, 1921; Seligmann, *Zeits. f. techn. Physik*, **6**, 237, 1925; Meissner, *Zeits. f. Physik*, **18**, 12, 1923.

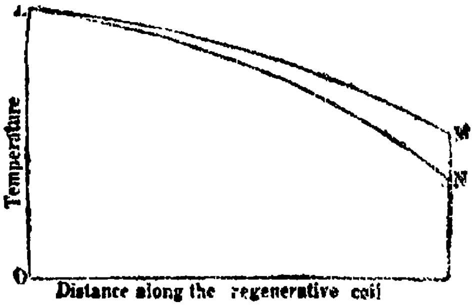

Fig. 13.—Temperature distribution in Regenerative Cooling.

12·20. The Joule-Thomson effect was for long a matter of pure academic interest, but it formed the basis of a great industry when Linde in Germany (1895) and Hampson in England (1895) almost simultaneously discovered, as stated above, that the JT-cooling can be used regeneratively, ultimately leading to production of temperatures low enough for liquefaction of air. The discoverers soon placed on the market 'Air liquefiers' which, though they have since undergone some modifications, are extensively used all over the world. A few types of air-liquefying machines are described below.

12·21. The Hampson Liquefier.—The special feature about it is the Hampson spiral. The high-pressure inflowing gas passes through copper tubes coiled in the form of concentric spirals arranged in layers; it then suffers the throttle expansion and becomes cooled. This cooled air rises through the interstices between the layers of the spiral and thereby cools the incoming high-pressure gas. After some time the high-pressure gas becomes sufficiently cooled so that on suffering the throttle expansion, it liquefies. The apparatus differs from that of Linde only in the manner of cooling the incoming gas. The apparatus was later improved by Olszewski.[1] The Hampson construction was utilized later by Dewar (Fig. 16), Onnes (Fig. 17) and Meissner for liquefying hydrogen and helium.

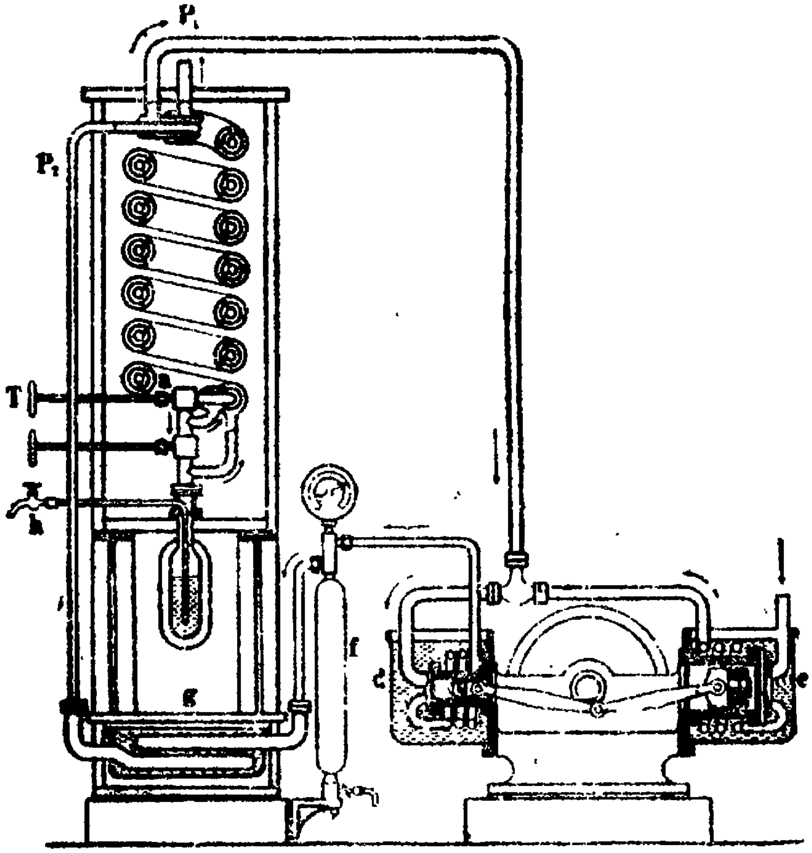

Fig. 14.—Linde's apparatus for liquefying air.

12·22. The Linde Liquefier.—Fig. 14 shows a commercial form of Linde's machine; *e*, *d*, is a two, or better three-stage compressor, the machine *e* compressing the gas from 1 to 20 atmospheres while machine *d* compressing it from 20 to 200 atmos. A charge of atmospheric air is taken at *e* and then compressed by *e* to 20 atmos. It is then cooled by passage through water-cooled tubes and is delivered to the suction side of the second-stage compressor. The compressed gas then passes through the stout cylinder *f* which contains caustic soda. This absorbs the carbon dioxide (if this is not done, carbon dioxide will become solidified and choke the valves in the liquefier proper). The gas next passes through the tubes *g* which are cooled by a freezing mixture to −20°C. From here it passes on through the metallic tubes P_2 to the inner tube of the liquefier. At *a* we have got the plug which is a throttle valve operated by the handle T. As the gas expands (in the first stage to 20 atmos.), the temperature falls to about −78°C., and the air again passes up through the middle tube cooling the incoming gas; it is then led through the pipe P_1 to the second stage compression cylinder, where it is again compressed and allowed to pass though the refrigerator *g* and the inner coils to *a*. After the completion of a few cycles the temperature of the incoming gas falls so low that the second throttle valve is opened. The air now expands to 1 atmosphere when it becomes liquefied due to Joule-Thomson cooling and collects in the Dewár flask, from which it can be removed by the siphon *h*. The unliquefied gas goes up through the outer-most tube cooling both the inner tubes. Fresh charge of air is being continuously taken in at *e*, compressed and delivered along with the gas from the middle tube to *d*. The process is cyclic.

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[1] *Ann. d. Physik*, **10**, 768, 1903.

12·23. Efficiency of Linde and Hampson Liquefiers.—Let us now give a brief discussion of the efficiency of these machines. We shall suppose that a steady state has been reached.

As discussion in §12·19 shows, the air at pressure p_e, temperature T_e enters the valve C, and expands to pressure p_d, and falls to temperature T_d. A part x is liquefied and collects at the bottom, while the remaining part goes through the outer coils at pressure p_f, temperature T_f. In the steady state $p_d = p_f$ and if the interchanger is perfect, $T_e = T_f$. Equating the enthalpy on the two sides of the plug we have

$$H_e = (1-x) H_f + x H_d, \quad \ldots \quad (31)$$

where H_e, H_f, H_d are the heat functions of the gas at E, F and the liquid at D respectively. Or

$$x = \frac{H_f - H_e}{H_f - H_d}. \quad \ldots \quad (32)$$

The state 'D' is predetermined because it corresponds to the boiling point of the liquid at a pressure of 1 Atmos. Let us suppose that the state 'F' is also prescribed. Then the only variable quantity is the state 'E' and x will be maximum when H_e is minimum, or $(\partial H_e/\partial p)_T = 0$.

Now since $\left(\frac{\partial H}{\partial p}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H = -\mu C_p$ (see page 286), the maximum efficiency is obtained when the input pressure and temperature are on the inversion curve of the differential JT-effect. Such curves were determined for air by Hausen (1926), and p_e, T_e are accordingly adjusted.

Actually, the problem of determining the optimum conditions for liquefaction of air as well as of H_2 and He are far more complicated, and the inquisitive reader is referred to original sources.[1].

12·24. The Claude and Heylandt Liquefiers.—These liquefiers combine adiabatic expansion doing external work as described in §12·6 and Joule-Thomson expansion. As one sees from Exercise 3, §12·17 the cooling produced by JT-expansion is much less than that produced by adiabatic expansion with external work, but on account of technical difficulties, adiabatic cooling could not be made continuous.

The main difficulty is presented by the fact that if we allow the compressed gas to do work, by allowing it to expand adiabatically in a cylinder, the temperature of the gas falls to a very low value and the lubricating oil in the moving parts of the piston becomes solidified and the piston becomes jammed. This was overcome in earlier machines by Claude by using some hydrocarbon such as petroleum ether as lubricating oil. This remains viscous at temperatures of $-140°C$ or even $-160°C$ and thus acts as an effective lubricant upto this range. Thus the critical temperature of air ($-140°C$) could be easily reached. Claude's apparatus is diagrammatically represented in Fig. 15.

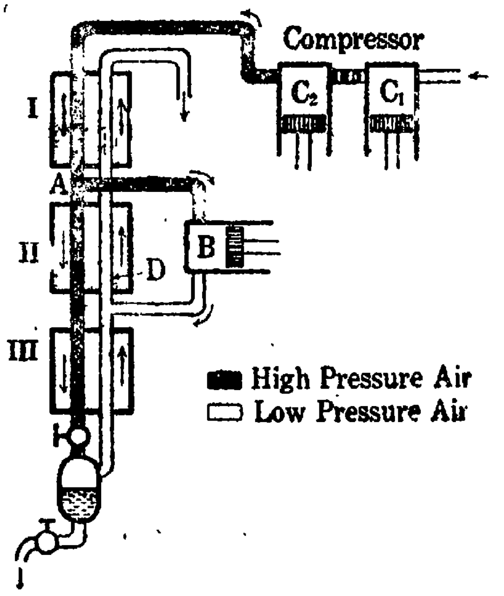

Fig. 15.—Claude's Air-Liquefying Machine.

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[1] The reader may consult *Low Temperature Physics* by L. C. Jackson,

By means of the compressors, air is compressed to 40 atmos. and passes through the heat-exchanger I where it is precooled by the out-flowing expanded gas to −80°C. Then it divides in two streams at A, a fraction x passing through the heat exchangers II and III to the throttle valve, and the remaining part $(1-x)$ going through the expansion engine B. The gas expands here to 1 atmos. sometimes through several stages, and this work is spent partly on driving the compressors. The cylinder is heat-insulated and the piston is kept gas-tight in later machines by a special type of impregnated leather cup which requires no further lubrication. The cooled gas passes through II and thus brings down the temperature of the fraction x of the gas traversing the exchanger II to a temperature considerably lower than the critical temperature, but not as low as its normal boiling point. The fraction x on account of its high pressure and low temperature condenses in exchangers II and III and then suffers J. T. expansion in the throttle valve to 1 atmos. A portion of the liquid evaporates in this last expansion on account of the pressure drop and the vapour returns to the compressor via the heat exchangers while the rest collects down as liquid.

The Heylandt liquefier differs from Claude's liquefier only slightly in matters of detail. In Heylandt liquefier the heat exchanger I is omitted and a smaller fraction of the gas enters the expansion engine though its initial pressure is higher. The Heylandt engine is not heat-insulated and therefore ordinary lubrication can be used. The temperature of the air leaving the Heylandt engine is above the critical temperature and further cooling of the gas is obtained by using the Joule-Thomson effect regeneratively.

It is obvious that an expansion turbine will possess several advantages over the reciprocating engine. Recently Kapitza[1] has produced an air liquefier working on Claude principle in which work is done on an expansion turbine, expansion being from 5·6 to 1·5 atmos. The machine embodies several novel features and is very convenient as all danger due to high pressure is eliminated.

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[1] *J. Phys. (U. S. S. R.)*, **1**, 7, 1939; *Nature*, **148**, 14, 1941.

12·25. Liquefaction of Hydrogen.—The problem of liquefaction of H_2 was a long challenge to science. The method of cascades which was first tried proved unsuccessful. Wroblewski thereupon studied the isotherms of hydrogen at low temperatures, and with the aid of equations (p. 407) calculated a and b, and thence the critical constants (p. 409). The critical temperature was found to be very low (−240°C) and Olszewski pointed out that this temperature could not be reached by the evaporation of liquid nitrogen, which was the most intensive cooling agent then known. The physicists then turned to the Joule-Thomson method.

The JT-expansion at ordinary temperature is inapplicable for the liquefaction of H_2 and He as stated in §12·15. Theoretical considerations based on the experimentally determined values of a and b showed that for H_2, $T_i = 2a/bR$ was abnormally low, viz., −73°C. It was clear that these gases had to be sufficiently precooled. Obszewski[1] found experimentally the inversion temperature for H_2 to be −79°C. For practical purposes an input temperature of 80° to 60°K, and input pressure of 160 Atmos was found satisfactory. For reaching these temperatures, precooling by liquid air ($T = -194$°C) is needed.

By using JT-effect, hydrogen was liquefied by Dewar[2] (1902), Travers[3] (1903), Nernst[4] (1911), Kamerlingh Onnes[5] (1906) and Meissner[6] (1925). A typical H_2-liquefier is shown in fig. 16.

Hydrogen prepared from zinc and sulphuric acid is compressed to about 150 atmos. and then passed through coils immersed in water in order to deprive the gas of the heat of compression. Next it passes through cylinders of caustic potash and some dehydrating agent and is deprived of its carbon dioxide and moisture. This is essential as these impurities would solidify much before the liquefaction of hydrogen sets in and choke the tubes. The gas then enters the liquefier and traverses the regenerative coils A (Fig. 16) which are cooled by the outgoing cold hydrogen gas, and in the final steady state, becomes cooled to about −170°C. Next the gas passes through a refrigerating coil B immersed in liquid air and then through another refrigerating coil C immersed in liquid air boiling at a pressure of 100 mm. This is adjusted by allowing liquid air from F to trickle into G and by evacuating G through a pump attached at P. The temperature of the hydrogen gas thus falls to about −200°C. After this it traverses the coil D and suffers Joule-Thomson expansion at the valve *a* which is operated by H. The gas thus becomes cooled and this cold gas passes up, round the chambers G and F thereby cooling the coils D and C, to the chamber R and from there to the compressor. Thus after a few cycles the temperature of the incoming gas at *a* falls to −250°C and on suffering further the Joule-Thomson expansion it liquefies and drops as liquid into the Dewar vessel V.

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[1] *Nature*, **65**, 576, 1902.

[2] *Jour. Chem. Soc.*, **73**, 529, 1898; *Comptes Rendus*, **126**, 1408, 1898; *Chemical News*, March, 1900.

[3] *Phil. Mag.*, April 1901, p. 411; *Nature*, **67**, 443, 1903.

[4] *Zeits. f. Electrochemie*, **17**, 735, 1911.

[5] *Leiden Commun.*, No. 94*f* (1906).

[6] *Naturwissenschaften*, **13**, 695, 1925; *Phys. Zeits.*, **26**, 698, 1925.

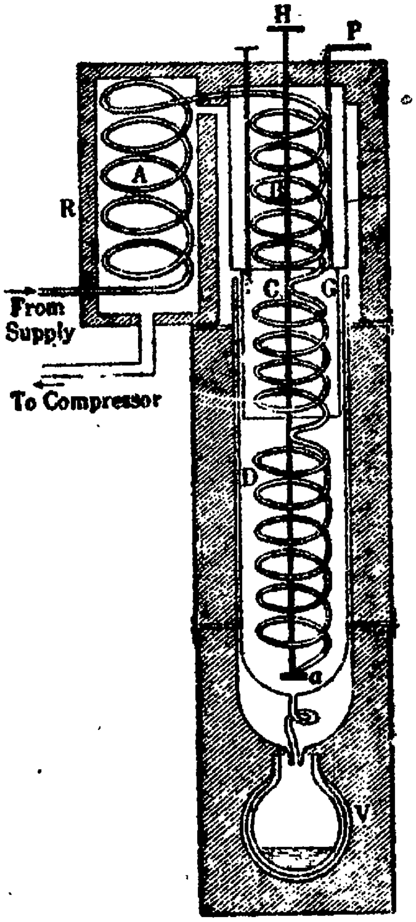

Fig. 16.—Hydrogen liquefying apparatus.

Liquid hydrogen boils at −252·76°C under atmospheric pressure. By causing it to boil under reduced pressure it can be frozen to a white solid.

12·26.—Liquefaction of Helium.—The liquefaction of helium forms a still more thrilling chapter than that of hydrogen, for it appeared to defy all known methods. Dewar attempted to obtain liquid helium by allowing highly compressed helium, which had been pre-cooled by solid hydrogen, to expand suddenly, but his efforts were fruitless. Olszewski's attempts were also unsuccessful, but more recently Simon[1] produced appreciable quantities of liquid helium by this method.

The credit for the successful onslaught on helium belongs entirely to Kamerlingh Onnes, for long director of the Cryogenic Laboratory at the University of Leiden, who proceeded in his efforts very systematically. He studied the isotherms of helium down to liquid hydrogen temperatures (up to -259°C) and obtained the critical constants for helium. He found the following values :—$T_c=5\cdot25$°K, $p_c=2\cdot26$ atmos. and normal boiling point $4\cdot26$°K. The Joule-Thomson inversion point came out to be about 35°K and the Boyle point 17°K. This temperature could therefore be reached only by pre-cooling the gas with liquid hydrogen. Kamerlingh Onnes was thus convinced of the possibility of being able to liquefy helium by the Linde process, and finally succeeded[1] in his efforts in 1908.

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[1] *Zeits f. Physik*, **81**, 816, 1933; *Rev. Sci. Instr.*, **10**, 251, 1939.

The apparatus used at the cryogenic laboratory at Leiden for the liquefaction of helium is very similar to the hydrogen liquefier employed there. We shall describe the new apparatus[2] erected in 1922 instead of the old classical apparatus with which Kamerlingh Onnes first succeeded in liquefying helium in 1908. The former is shown in Fig. 17. As helium is rather costly, the arrangement is to be such that it can work in cycles. Gaseous helium, compressed to 36 atmos. enters at A and divides into the two spirals B, B′. Then the two streams again unite and again divide and pass through the two spirals C and C′. B and C are cooled by cold hydrogen vapour, B′, C′ by cold helium vapour. The streams again unite, and pass through the spiral D, which is cooled by the cold, hydrogen vapour, supplied from liquid hydrogen in H_2, which is always kept replenished from the H_2 reservoir on the left. Lastly the gas passes through the spiral F which is surrounded by the cold outgoing helium vapour. At K the Joule-

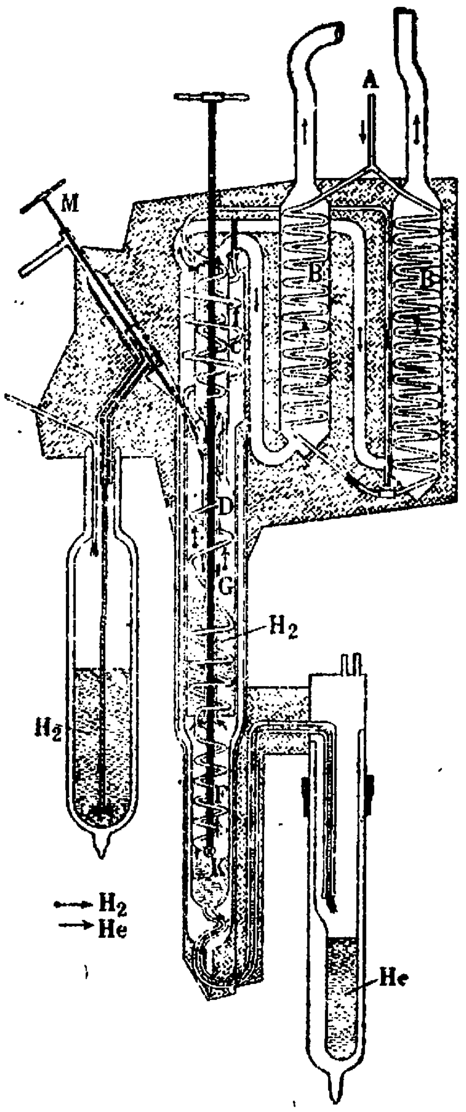

Fig. 17.—Kamerlingh Onnes' apparatus for liquefying helium.

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[1] *Leiden Commun.*, No. 108 (1908) ; *Nature*, August, 1908.

[2] *Leiden Commun.*, *Suppl.*, 45 (1922).

Thomson expansion takes place and helium becomes cooled. This cold gas traverses round the spiral F, through the straight tube G, round the spirals C′ and B′ back to the compressor. After a few cycles the gas becomes liquefied and passes through the tube to the cryostat where it is collected.

In Onnes' original experiment helium was obtained from monazite sand obtained from the Travancore coast in India. Monazite is still one of the best sources of helium, but later, helium has been found occurring in many natural gas deposits particularly in Texas. At the present time there are quite a number of helium liquefiers in the world, though until 1923 Leiden was the only place in the world having a helium liquefier. McLennan[1] constructed a helium liquefier at Toronto in 1923 and Meissner[2] at Berlin in 1925.

12·27.—Liquefaction of Hydrogen and Helium by the Claude-Heylandt Method (Kapitza, Collins).—The use of the Claude or Heylandt's method, so successful in the liquefaction of air, appeared to fail for H_2 or He, as all lubricants get stiff at these temperatures. But Kapitza[3] overcame this difficulty by discarding lubricants altogether.

The main feature of his engine is that the piston is loosely fitted in the cylinder with a definite clearance of 0·04 mm. so that when the gas is introduced into the cylinder at high pressure, it can escape freely through the gap between the piston and the cylinder The expansion engine is arranged in such a way that the piston moves very rapidly on the expanding stroke, and the entire expansion takes place in such a short time that the amount of gas escaping through the gap is very small and inappreciable.

The cooled gas obtained by this adiabatic expansion is then allowed to cool a portion of the incoming high pressure gas as in Claude's air liquefying apparatus. Thus the latter becomes much cooled and during the final stage, the cooled gas is allowed to undergo Joule-Thomson expansion as in Heylandt's method and becomes liquefied.

The great advantage of this method is that no precooling with liquid hydrogen is necessary as in the Linde process, so that no additional liquefaction apparatus for producing liquid hydrogen is required and the attendant risks are thereby eliminated. The method has been further developed by Collins[1] who has been able to place on the market a commercial machine designed to produce liquid helium with ease and safety of operation and liquid helium could be easily drawn off for use in external dewars. There are more than seventy such machines installed in laboratories throughout the world making cryogenic research possible even in non-specialist laboratories. The Collins cycle makes use of expansion engines at two successive stages followed by a Joule-Thomson expansion at the final stage.

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[1] *Nature*, **112**, 135, 1923. [2] *Naturwissenschaften*, **13**, 695, 1925.

[3] *Proc. Roy. Soc. Lond.* **147**, 189, 1934; *Nature*, **133**, 208, 1934.

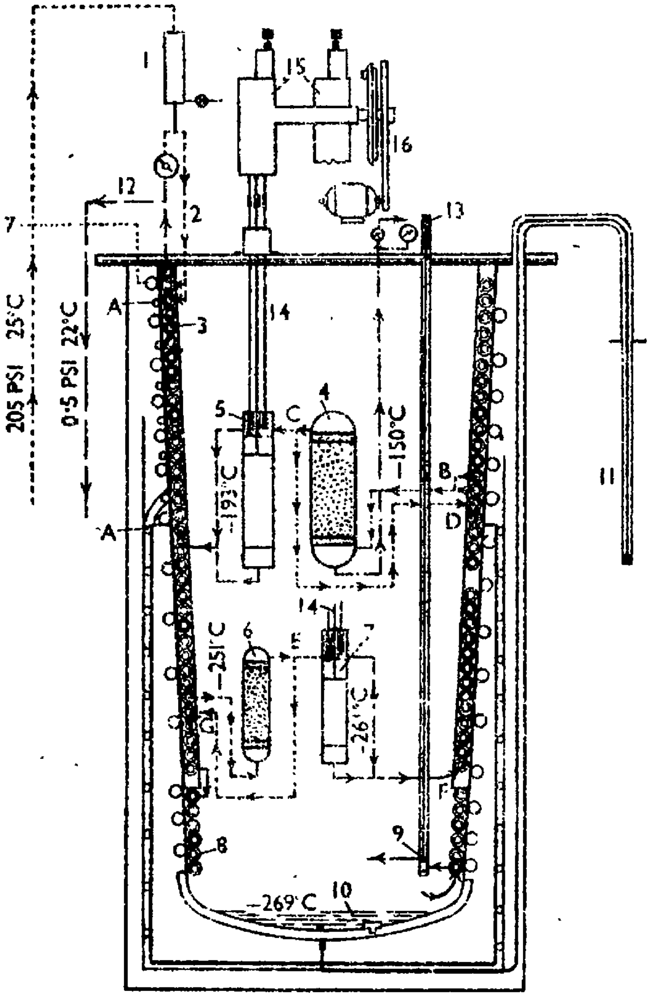

Fig. 18.—Flow diagram of Collin's Liquefier (Not to scale).

Fig. 18 shows the flow diagram[2] of the Collin's cycle. Helium from a gas-holder is compressed to a pressure of about 15 atmospheres by a special four stage helium compressor which has a low compression ratio so that impurities due to lubricating oil are negligible. The compressed helium is cooled by cooling water, then passes through an oil separator and fine glass wool filter, and finally enters the liquefier through (2) and traverses the specially designed heat exchangers (3). These consist of a cupro-nickel tube with rectangular copper fin wound edgewise into the tube and solder-bonded throughout its entire length, this fin-tube being coiled helically on a stainless steel conical shell which is inserted into a larger shell to provide an annular space for the low pressure returning helium. The compressed helium thus flows in the fin-tube counter-current to the returning expanded helium, and gets thereby cooled, finally emerging at B at a temperature of about −150°C in the steady state. Then it passes through the pot (4) containing activated coconut charcoal powder which removes the remaining traces of impurities from the gas. About one-fifth of this compressed helium is expanded isentropically in the first expansion engine (5) and gets cooled to −193°C and passes up through the heat exchanger (3) cooling the incoming gas, while the remaining four-fifths of the high pressure gas re-enters the heat exchangers at D and continues to flow down till it gets cooled to about −251°C. Then it is passed through the second charcoal pot (6) and again divides at E into two parts; the larger portion (about three-fifths) suffers isentropic expansion in the second expansion engine (7) becoming thereby cooled to about −261°C and then enters the annular space of the heat exchange at F to combine with the outgoing low pressure helium. The remaining two-fifths of the high pressure helium re-enters the heat exchanger at G to traverse the lower end of the fin-tube exchanger and finally enters the Joule-Thomson heat exchanger (8) which consists of two concentric tubes arranged helically, the high pressure helium flowing through the annulus and finally expanding at the Joule-Thomson expansion valve (9) which is operated by the knob (13). About one-tenth of this gas liquefies and collects at (10) from where it can be drawn off through outlet (11), while the remainder enters the low pressure side of the heat exchanger to join the exhaust streams from the expansion engines and return through (12) to the compressor for being recycled. Precooling by liquid nitrogen through auxiliary precooling coils A may be utilised to reduce the starting time and increases the yield of liquid helium. Other gases like hydrogen can be liquefied in an auxiliary cooling coil system (17) by merely cooling under ordinary pressure.

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[1] *Rev. Sci. Inst.*, **18**, 157, 1947.

[2] Figs. 18 and 19 and the description of Collins liquefier have been taken from the manual of ADL Collins Helium Cryostat with the kind permission of Messrs Arthur D. Little Inc., Cambridge (Mass.).

The chief part of the liquefier is the expansion engine which has to be carefully designed to meet several unusual requirements. It is important that the seal between the piston and cylinder be good but it is impossible to use a lubricant for sealing as it will freeze. This is achieved in the Collins expansion engine by constructing the piston and cylinder of nitrided nitralloy steel and leakage is controlled by the extreme fitting of piston to cylinder, the clearance being about 0·0005 inches on the diameter, and the operation being completely dry. A cross-section of the expansion engine is shown in Fig. 19. The piston has the customary circumferential grooves to equalise any pressure differences which might produce a side thrust and thus the gas seal is improved and the piston kept centred. The piston is joined loosely to the piston rod so that the piston is self-aligning. The engine is arranged for single-acting operation so that the piston rod is in tension at all times, thereby permitting the use of a long slender rod with minimum cross-section to minimise heat leakage. The valves are also operated by long slender pull rods which have to overcome the closing force of heavy alloy steel springs. The piston and valve rods (14) pass at the top through leak-proof stuffing boxes which are specially designed and sealed with neoprene and a slight amount of lubricating oil. The ends of these rods are connected to a cam-operated cross-head mechanism which serves to regulate the stroke of the piston and the timing of the valves. At the proper instant the high pressure helium entering the engine by the intake tube suffers isentropic expansion at the valve and the expanded gas is later driven out through the exhaust valve during the upward stroke of the piston. This expanded gas together with the gas leaking through the clearance space goes out to the suction side of the compressor.

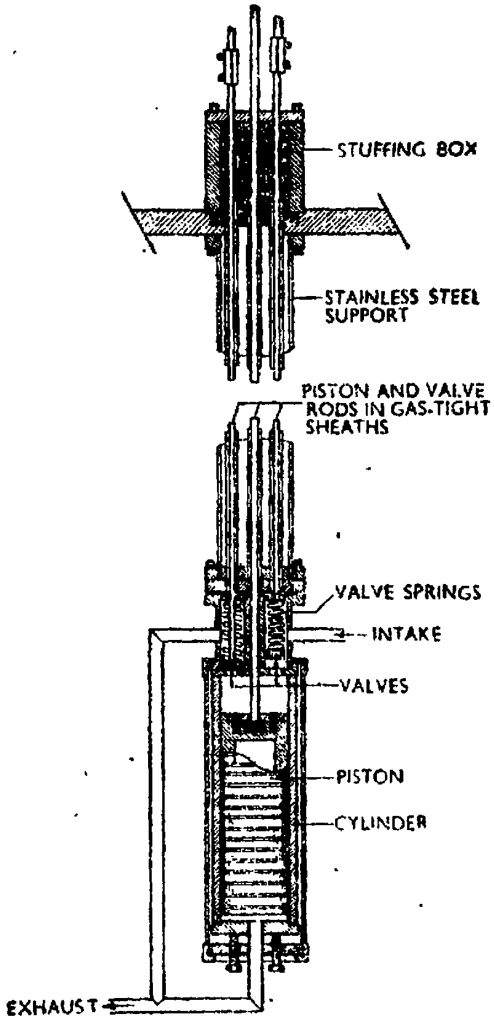

Fig. 19.—Cross-section of the Expansion Engine.

12·28. Other Helium Liquefiers.—Helium has also been liquefied by first cooling the high pressure helium gas with solid hydrogen and then allowing it to expand adiabatically. This is usually done in the Simon expansion bomb and such liquefiers are frequently used in Oxford for producing small quantities of liquid helium.

Fig. 20 shows the detailed working of such a liquefier. Helium is compressed through the tube (1) into the bomb A to a pressure of about 150 atmos. and is cooled to the temperature of the liquid hydrogen H, kept in the external dewar, by conduction through helium gas contained in the metal case C at a few centimetres pressure. Liquid hydrogen is also introduced through the tube (3) into the box B which sits on A. Next the case C is highly evacuated through tube (2) so that A is thermally insulated, and hydrogen in B is pumped by a suction pump connected to (3) so that it solidifies producing a temperature of about 11°K. By opening a valve the compressed helium is now allowed to expand via (1) into a gas-holder at a pressure of about 1 atmos. The expansion is carried out slowly in about 5 to 20 minutes and takes place adiabatically due to the excellent heat insulation. It is, therefore, almost quite reversible and produces considerable cooling in A so that a large part of the helium (about 80% of the total volume) remains in A as liquid. The chief reason for this large yield is that the density of the compressed helium gas is about 50 per cent greater than the density of liquid helium at 1 atmos. pressure.

For carrying on experiments helium gas at a pressure of about 1½ atmos. is forced through tube (4), which is soldered to the side of A, into the experimental vessel D where it liquefies. D can be maintained at any temperature between 1° and 4·2°K for about four hours by a single condensation in A. The lower parts of D and C may be made of glass if it is necessary to see the apparatus and the liquid helium in D.

Simon desorption method.—Simon proposed a novel method for producing temperatures low enough for liquefaction of He by rapid pumping out of gas adsorbed on charcoal at 14°K. This process is analogous to evaporation and is similarly accompanied by cooling. The method is still useful for producing temperatures in the difficult region between 10°K and 4·2°K but is now seldom used for liquefying helium.

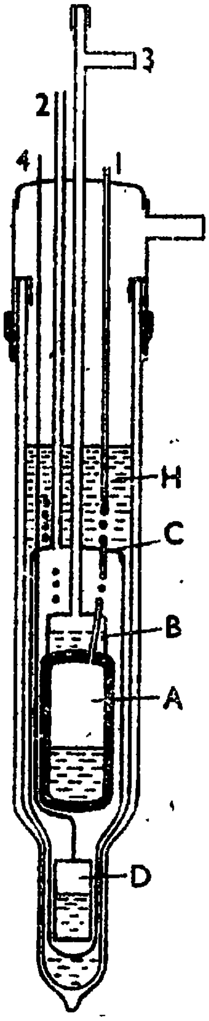

Fig. 20.—Simon Expansion-Bomb Helium Liquefier.

PRODUCTION OF TEMPERATURES BELOW 4°K

12·29. Solidification of Helium.—Kamerlingh Onnes tried to solidify helium by reducing pressure, but though he claimed to have reached 1·15°K in 1910, helium still remained a fluid. In 1921 he again tackled the problem and by employing a battery of large diffusion pumps he reduced the vapour pressure to 0·013 mm. and the temperature to 0·82°K, but helium still remained fluid. After the death of Onnes, his collaborator and successor, Dr. Keesom succeeded in solidifying helium by subjecting it to an enormous pressure. Helium was compressed in a narrow brass tube under a pressure of 130 atmospheres, the tube itself being immersed in a liquid helium bath. It was found that the tube was blocked indicating that part of the gas had solidified. If the pressure was reduced by 1 or 2 atmospheres, the tube became clear again. Later experiments showed that helium at 4·2°K solidified at 140 atmospheres while at 1·1°K it solidified only under 23 atmospheres. The solidification curve of liquid helium was obtained by Keesom and others and is shown in Fig. 21 in which all portions are not on the same scale. It gives the corresponding pressures and temperatures at which solid helium is in equilibrium with liquid helium. Simon[1] has extended the curve to 5600 atmos., the melting point rising to 42° K, the solid and vapour thus being in equilibrium above the critical point. Solid helium can hardly be distinguished from the liquid; it is a transparent mass having almost the same refractive index as the liquid.

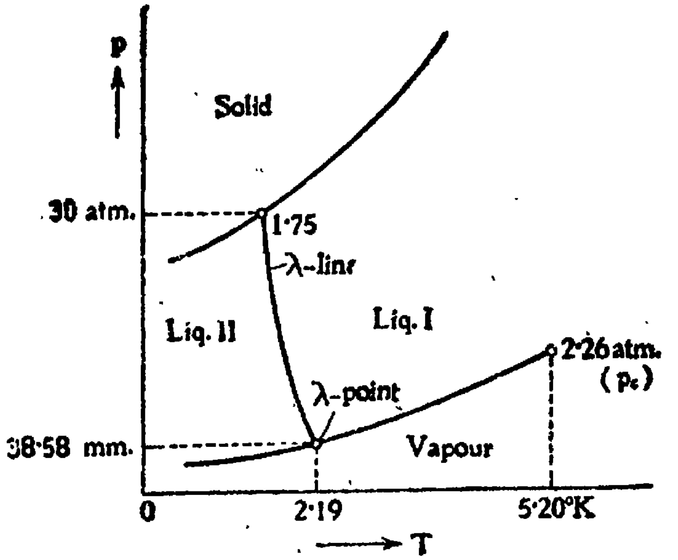

Fig. 21.—Phase diagram of helium (ordinate not to scale.)

Pursuing the vapour pressure curve down to lower temperatures it is seen that the gas and the liquid continue in equilibrium down to the absolute zero of temperature i.e., the three phases solid, liquid and gas are never found to coexist. This is an extraordinary thing and shows that helium is a unique liquid. The vapour pressure data have already been discussed in §1·24.

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[1] *Zeits. f. Phys. Chem.* B, **6**, 62, 1929.

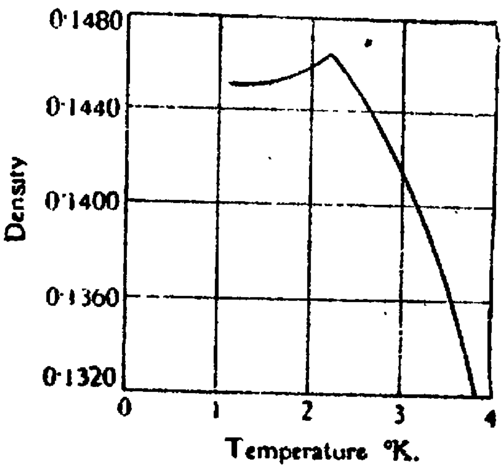

Fig. 22.—Variation of density of liquid helium with temperature.

12·30. Liquid Helium II.

—In course of his classical investigations on helium, Kamerlingh Onnes and Boks[1] (1922) had found that liquid helium appears to show certain discontinuities in its density when it is cooled by evaporation to about 2·18°K (Fig. 22). The density rises by about 20% as T falls from 4·2°K to 2·19°K, reaching a maximum of 0·1462 at 2·19°K, and then decreases with decrease of temperature. Keesom[2] found discontinuities in the dielectric constant and the specific heat of liquid He in equilibrium with its saturated vapour (Fig. 23). The temperature of 2·19°K at which the discontinuity appears is called the lambda point on account of the shape of the specific heat—temperature curve. When liquid helium is being evaporated rapidly

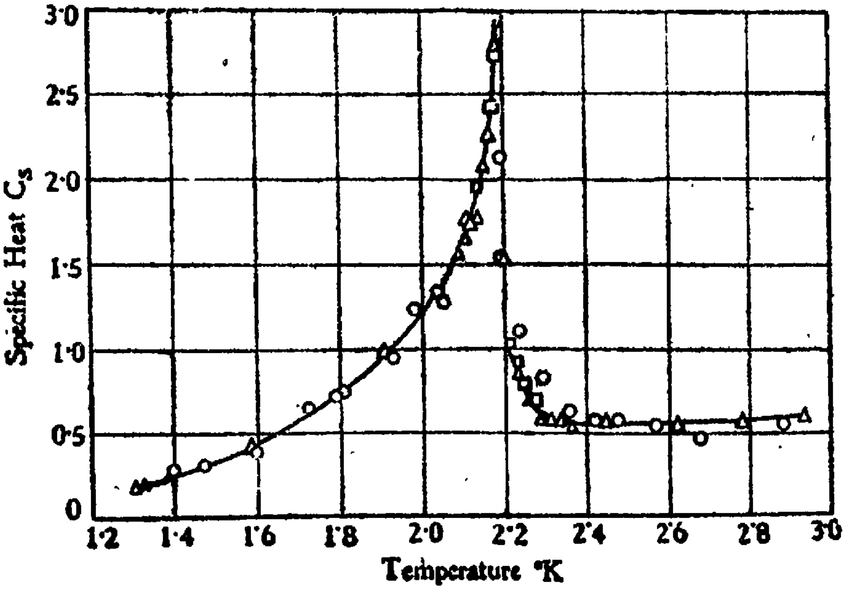

Fig. 23.—Specific Heat of liquid helium (saturated) at different temperatures.

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[1] *Leiden Commun.*, No. 170*b*. [2] *Ibid.*, Nos. 192*a*. 219*e*, 221*d*.

by fast pumping, it gets cooled and boils vigorously. But as soon as the lambda point is reached (Fig. 21) according to Wilhelm, Misener and Clark working at Toronto, boiling stops and the liquid appears to be absolutely quiet. This led to the postulate that a new liquid phase of helium, now called He II, is formed below the lambda point. Keesom and Clusius[1] observed the cooling of helium by placing a certain quantity of it in a liquid helium bath in which the temperature could be lowered progressively. By adjusting the pressure in the sample, they could find out the cessation of boiling at definite pressures, and thus the p/T-curve He I to He II (called the λ-line) was obtained (Fig. 21). It meets the He I (liquid)/ He (solid) curve at $T = 1 \cdot 743$, $p = 29 \cdot 09$ atmos. where the solidification curve shows a bending. The point of intersection of the two curves is a triple point where He solid, He I liq. and He II liq. can coexist. The lambda line liq. He I/ liq. He II is continued from this point to the lambda point ($T = 2 \cdot 19$°K, $p = 0 \cdot 0508$ atmos.) where He I, He II and vapour of He co-exist.

We have considered above some of the thermal properties of liquid helium II. The most remarkable properties of helium II are however exhibited when it is flowing and not when it is stationary. These dynamical properties along with the nature of liquid helium II are discussed later in Note 17.

12·31. Thermodynamics of λ-transition.—We have described above some of the thermal properties of liquid helium I and liquid helium II. The shape of the specific heat curve in fig. 23 is similar to that observed in the case of ferro-magnetic substances near the Curie point where the ferromagnetism disappears or in the case of alloys where an ordered arrangement changes into disorder. This is ascribed to the fact that below 2·19°K liquid helium is in a more ordered state than above that temperature. The latent heat of vaporization of liquid helium has been determined by Dana and Kamerlingh Onnes and is found to show no sudden jump at 2·19°K. These considerations show that the λ-transition is not an ordinary phase transformation of the first order which is accompanied by a discontinuous change in entropy and specific volume (Sec. 8·16). It will be noticed that here the derivatives of entropy with respect to temperature and pressure i.e., specific heat and coefficient of thermal expansion α_S at the saturation vapour pressure change discontinuously. The λ-transition is therefore called *second order phase transition.*

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[1] *Leiden Commun.*, No. 216*b*.

Applying the theory developed in §8·16 for second-order phase transitions we have, as proved there,

$$\frac{dp}{dT}=\frac{C_{p_2}-C_{p_1}}{Tv(\alpha_2-\alpha_1)} \quad . \quad . \quad . \quad . \quad . \qquad (33)$$

and

$$\frac{dp}{dT}=\frac{\alpha_2-\alpha_1}{\kappa_2-\kappa_1} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (34)$$

Taking the experimental values for He I and He II, $C_{p_1}=1{\cdot}2$, $C_{p_2}=2{\cdot}9$ cal./gm. deg., $\alpha_1=\cdot 02$, $\alpha_2=-0{\cdot}04$ deg.$^{-1}$ $v_1=v_2=6{\cdot}84$ cm^3/gm., $T=2{\cdot}19°$ we get from (33) $dp/dT=-78$ atm./deg. which agrees well with the experimentally observed value $-81{\cdot}9$ atm./deg. Using the equation (34) we get for the change of compressibility the value $-6{\cdot}2\times 10^{-10}$ which is too small to be measured accurately.

12·32. Properties of Bodies at Liquid Helium Temperatures.

—The properties of material substances undergo very interesting changes at liquid helium temperatures. For example, K. Onnes[1] found in 1911 that at about 4°K many metals appear to lose completely their electrical resistance, and become superconductors.[2] This is illustrated in Fig. 24 which represents the variation of the resistance of mercury with temperature. The resistance does not absolutely vanish but falls by about a million times so that if a current be induced in a coil of the solidified metal placed inside such a bath by bringing a magnet near it, the current does not immediately die out, as in ordinary electromagnetic induction, but may continue to flow for days together. This is because the current induced in a coil decays according to the law $i=i_0e^{-(R/L)t}$ where R is the resistance of the coil and L its self-induction.

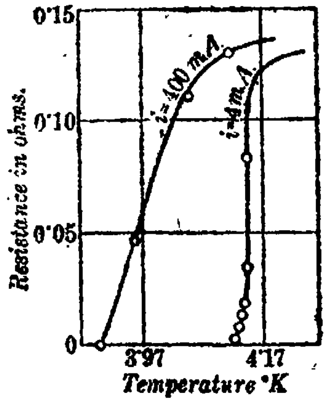

Fig. 24.—Resistance of mercury near the absolute zero.

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[1] *Leiden Commun.* Nos. 122*b*, 124*c*, 1911.

[2] For a good account of superconductivity, see *Superconductivity* by D. Shoenberg, Cambridge University Press (1952); or *Theory of Superconductivity* by M. von Laue, New York, Academic (1952).

Generally L/R is extremely small, say one hundredth of a second, but near the absolute zero, R suddenly diminishes million times while L which depends only on the geometry of the coil remains unchanged, hence L/R becomes about 10^5 sec. Hence the current takes several days to die out completely.

Besides this, it has been found that near the absolute null point, the specific heat, the heat conductivity etc., seem to vanish. On account of the interest created by these discoveries, attempts have been made in recent years to reach closer to the absolute zero and investigate the thermal, electric and magnetic properties intensively over an extended range of temperatures. This has yielded some very interesting results and has increased considerably our knowledge of the nature of these phenomena. For details see Squire, *Low Temperature Physics* (1953).

MARCH TOWARDS ABSOLUTE ZERO

12·33. Cooling produced by Adiabatic Demagnetisation of Paramagnetic substances.

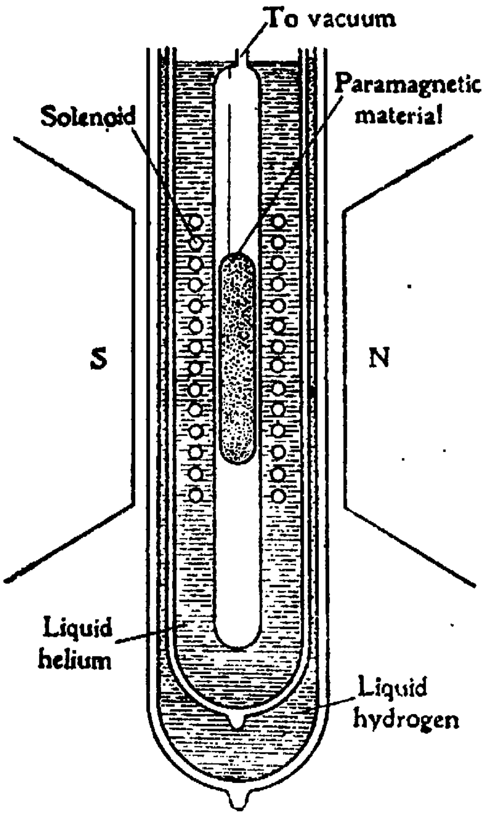

Fig. 25.—Apparatus for producing cooling by adiabatic demagnetisation.

12·33. Cooling produced by Adiabatic Demagnetisation of Paramagnetic substances.—Up to 1925 the only method available for producing temperatures lower than 4°K was the boiling of liquid helium under reduced pressure. Using this method Keesom reached 0·726°K in 1932 by using a battery of diffusion pumps of high sucking capacity. (The vapour pressure of helium was in this way reduced to $3{\cdot}6\times10^{-3}$ mm. of mercury). It was found almost impossible to push much further down with this method, as the sucking power needed increases exponentially with decrease of pressure.

In 1926, Giauque[1] and Debye[2] showed theoretically that temperature lower than the helium limit can be produced by the adiabatic demagnetisation of paramagnetic salts, and Giauque shortly afterwards demonstrated the cooling experimentally. Fig. 25 illustrates the experimental procedure. This is as follows :

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[1] *Jour. Amer. Chem. Soc.*, **49**, 1864, 1870, 1927.

[2] *Ann. d. Physik*, **81**, 1154, 1926.

(a) The paramagnetic salt, say Gadolinium sulphate $Gd_2(SO_4)_3 . 8H_2O$ is taken in the form of a powder and is first pressed into the form of a cylinder or prolate spheroid. It is then suspended on silk or nylon fibres inside a cylindrical chamber which is surrounded by a liquid helium bath and the latter vigorously pumped so that a temperature of about 1°K is obtained. During the pumping the salt is cooled down to the bath temperature by the exchange gas (helium at a pressure of about 0·1 mm. Hg) which had been introduced previously inside the cylindrical chamber. The bath itself is within the poles of an electromagnet.

(b) The magnetic field is now switched on, and the heat of magnetisation is conducted away by gaseous helium in the chamber to the He-bath outside.

(c) The chamber is now evacuated by a powerful pump to the highest vacuum, and the specimen is thus thermally isolated.

(d) The field is now entirely switched off, or reduced.

The temperature of the sample now falls. This fall in temperature is measured by determining the change in the paramagnetic susceptibility of the sample. To measure this quantity, the sample is surrounded by a close-fitting coaxial solenoid and the self-inductance of the coil is measured with the Anderson bridge. The value of the inductance gives the susceptibility.

Various modifications of the simple arrangement described above have been used in different laboratories. For the cryostat usually silvered glass dewars are used but some laboratories have metal cryostats. The separation of the magnet and cryostat after the demagnetisation is usually done by mounting the magnet on rails and wheeling it away after demagnetisation. Sometimes if the magnet is too big, the cryostat itself is moved out. The design of the cryostat depends upon the method adopted for producing liquid helium. Depending upon the nature of the experiment, the specimen is used as a single crystal ground in the desired shape or as a powder compressed to approximately the crystalline density or as small crystals loosely packed in a container. The sample tube may be made of metal or glass. This tube is either mounted on a thin-walled glass pedestal or suspended from taut fibres inside the chamber. For determining the susceptibility it is more usual to measure the mutual inductance either by a ballistic bridge or an A.C. bridge. In both of these a null method is utilised and the secondary voltages are balanced out by a variable mutual inductance. For relative merits of these modifications the reader may consult Gorter, *Progress in Low Temperature Physics*, Chap. XIV.

A complete theory of the phenomenon is rather complicated; the following is only a preliminary sketch:

According to the Curie-Langevin theory of paramagnetism, a knowledge of which is essential for the understanding of the phenomenon, a paramagnetic crystal like $FeCl_2$ consists of Fe^{++}-ions, each of which is a small atomic magnet surrounded by two Cl^{-}-ions, which are diamagnetic and can be left out of account. The Fe^{++}-ions, and Cl^{-}-ions are arranged in a crystal lattice, whose form is given by X-ray analysis. Normally the total heat energy of the crystal consists of vibrational energies of the ions (we may call this the lattice-energy), but when the crystal is put in a magnetic field, a new factor is introduced. The Fe^{++}-ions, which are small magnets with definite magnetic moment, and are, in the absence of the field, oriented at random, now tend to align themselves parallel to the field $\mathscr{H}$, and thus produce a resultant magnetic moment $\mathscr{I}$ per c.c. Working on the classical theory, Langevin deduced that the susceptibility χ, is given by

$$\chi = \frac{\mathscr{I}}{\mathscr{H}} = \frac{n\mu}{\mathscr{H}}\left(\coth\frac{\mu\mathscr{H}}{kT} - 1\Big/\frac{\mu\mathscr{H}}{kT}\right) = \tfrac{1}{3}\,\frac{\mu^2 n}{kT}\text{ approx.,} \qquad (35)$$

where μ is the magnetic moment of each paramagnetic ion, n= number of ions per c.c., χ=susceptibility per c.c.

The energy of magnetisation is given by $\frac{1}{2}\chi\mathscr{H}^2$ per unit volume. The total energy of the system is now made up of the lattice energy plus the energy of magnetisation.

Langevin, thus, gave a theoretical proof of the law discovered by Curie from his experimental studies that for many paramagnetic substances $\chi = C/T$ where C is a constant, called Curie constant. One of the best studied substances is the rare earth element Gadolinium whose salts were investigated by K. Onnes and his collaborators upto 1·3°K, and were found to obey the law $\chi = C/T$. But generally a modified law due to Weiss $\chi = C/(T-\theta)$ is found to give better accord with experiments, and in the case of Gd, up to 1·3°K.

Langevin's classical theory has been profoundly modified later, on account of the discovery of directional quantisation of ions, but for a fuller account see Saha and Saha, *Treatise on Modern Physics*, Chap. XV.

From what has been said it is clear that the thermodynamical behaviour of a paramagnetic crystal placed in a magnetic field depends, in addition to p and V, on the magnetising field $\mathscr{H}$ also. The usual thermodynamical relation

$$\delta Q = dU + pdV,$$

is now to be replaced by

$$\delta Q = dU + pdV - \mathscr{H} d\mathscr{M}, \quad . \quad . \quad . \quad . \quad (36)$$

because $-\mathscr{H} d\mathscr{M}$ is the magnetic work done by the substance, $\mathscr{H} d\mathscr{M}$ being the work done by the field in magnetising the substance. $\mathscr{M}$ is the intensity of magnetisation per gram molecule, hence, $\mathscr{M} = \chi V \mathscr{H}$ where χ is the susceptibility per c.c. From the second law the change in entropy dS is given by

$$TdS = dU + pdV - \mathscr{H} d\mathscr{M} \quad . \quad . \quad . \quad . \quad (37)$$

Besides p and V, we have now to use two more variables $\mathscr{H}$ and $\mathscr{M}$. $(-\mathscr{H})$ may be taken to play a rôle similar to that of p, and $\mathscr{M}$ that of volume. We have now

$$dU = TdS + \mathscr{H} d\mathscr{M} - pdV, \quad . \quad . \quad . \quad . \quad (38)$$

and just as in Chap. VII, p. 323, if x, and y are a pair of independent thermodynamical variables, we can deduce from the condition

$$\frac{\partial^2 U}{\partial x \partial y} = \frac{\partial^2 U}{\partial y \partial x}, \quad . \quad . \quad . \quad . \quad (39)$$

the general relation

$$\frac{\partial(T,S)}{\partial(x,y)} + \frac{\partial(\mathscr{H},\mathscr{M})}{\partial(x,y)} = \frac{\partial(p,V)}{\partial(x,y)}. \quad . \quad (40)$$

In these experiments on magnetisation the change in volume is negligible. We can therefore assume $dV = 0$, and $V =$ constant approximately. We have therefore

$$\frac{\partial(T,S)}{\partial(x,y)} = -\frac{\partial(\mathscr{H},\mathscr{M})}{\partial(x,y)}. \quad . \quad . \quad . \quad (41)$$

From this general equation, it is possible to deduce six thermodynamical relations by choosing two out of the four variables T, S, $\mathscr{H}$, $\mathscr{M}$ as independent but of these only two are important. These are obtained by putting (1) $x=\mathscr{H}$, $y=T$; (2) $x=\mathscr{H}$, $y=S$ respectively. They are

$$\left(\frac{\partial S}{\partial \mathscr{H}}\right)_T = \left(\frac{\partial \mathscr{M}}{\partial T}\right)_{\mathscr{H}}; \quad \left(\frac{\partial T}{\partial \mathscr{H}}\right)_S = -\left(\frac{\partial \mathscr{M}}{\partial S}\right)_{\mathscr{H}}. \quad . \quad (42)$$

Both relations will be used later, but for the present, we deduce from the second[1]

$$\left(\frac{\partial T}{\partial \mathscr{H}}\right)_S = -\left(\frac{\partial \mathscr{M}}{\partial S}\right)_{\mathscr{H}} = -\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{\mathscr{H}} \Big/ \left(\frac{\partial S}{\partial T}\right)_{\mathscr{H}}. \quad (43)$$

Now $T\left(\frac{\partial S}{\partial T}\right)_{\mathscr{H}} = C_H$, the specific heat of the substance under constant field. Hence we have

$$\left(\frac{\partial T}{\partial \mathscr{H}}\right)_S = -\frac{T}{C_H}\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{\mathscr{H}} \quad . \quad . \quad . \quad (44)$$

which gives the change in temperature during adiabatic magnetisation or demagnetisation. This phenomenon is sometimes called the *magnetocaloric effect.*

This equation can be at once applied to our case. We have, on integration,

$$T_f - T_i = -\int_{\mathscr{H}_i}^{\mathscr{H}_f} \frac{T}{C_H}\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{\mathscr{H}} d\mathscr{H}. \quad . \quad . \quad (45)$$

Here T_f = final temperature, T_i = initial temperature, $\mathscr{H}_i$, $\mathscr{H}_f$ are the initial and final fields. Since $\mathscr{M} = \chi \mathscr{H} V$, we have on putting $\chi = C/T$ (Curie's law),

$$T_f - T_i = \frac{CV}{\bar{C}_H T}\int_{\mathscr{H}_i}^{\mathscr{H}_f} \mathscr{H}\, d\mathscr{H}, \quad . \quad . \quad . \quad (46)$$

replacing C_H within the integral by its average value $\bar{C}_H$. This, though not justified, enables us to understand the course of events. Suppose we have $\mathscr{H}_f = 0$. The fall in temperature is now given by

$$-\Delta T = T_i - T_f = \frac{CV}{2T_i \bar{C}_H}\mathscr{H}_i^2. \quad . \quad . \quad (47)$$

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[1] This can be written down directly from eqn. (12) if we assume that $dV = 0$ in (38) and $-\mathscr{H}$ plays the role of p, and $\mathscr{M}$ that of V.

Table 6 shows the temperatures obtained by Giauque and Mac-Dougall on a sample of $Gd_2(SO_4)_3.8H_2O$ in a first series of experiments. $T_i = 1·36$°K.

Table 6.—Cooling produced by adiabatic demagnetisation of Gadolinium sulphate.

$\mathscr{H}$ in gauss	4575	6200	6860	7920
T_f ..	0·492	0·346	0·315	0·258
$-\Delta T$ ..	·868	1·014	1·045	1·102
$(\Delta T/\mathscr{H}_i^2)\times 10^8$..	4·15	2·64	2·22	1·76

N. B. Actually C_H varies with T and $\mathscr{H}$, and the procedure given here is only rough.

The measurement of the temperature in this region is a matter of great difficulty. What is actually done is to assume the validity of Curie's law, and calculate from the measurement of the susceptibility of the sample a Curie temperature (also called magnetic temperature) $T^* = C/\chi$. From the Curie-temperature the thermodynamical temperature T is determined by methods explained later.

Actual Results.—The method was tried by Giauque and Mac-Dougall[1] on Gd-sulphate who using a field of 8,000 oersteds, registered a fall to 0·25°K, starting from an initial temperature of 1·5°K. Since then a large number of experiments have been carried out at the cryogenic laboratories of Leiden (de Haas, Wiersma and Kramers[2]), Oxford (Kürti and Simon[3]). The lowest recorded Curie temperature is that by de Haas and Wiersma[4] (1935) who used mixed crystals of 1 chromium-potassium alum +14·4 aluminium-potassium alum and a field of 24,000 oersteds; and starting with an initial temperature of 1·29°K, they could go down to 0·0044 * (Curie temperature) which is found to be equal to 0·0034°K. More recently de Klerk, Steenland and Gorter[5] in Leiden working with powdered mixed crystals of chromium alum and aluminium alum reached the Curie temperature $T^* = 0·033$ which according to them corresponds to $T=0\cdot 0029°\text{K}$ but according to Oxford workers[1] it corresponds to $0\cdot 010°\text{K}$.

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[1] *Phys. Rev.*, **43**, 768, 1933.

[2] *Nature*, **131**, 719, 1933; *Physica*, **11**, 175, 1933.

[3] *Nature*, **133**, 907, 1934; *Physica*, **3**, 1107, 1934.

[4] *Physica*, 2, 335, 1935. [5] *Physica*, **15**, 649, 711, 1949.

12·34. Conversion of Magnetic Temperature into Kelvin Temperature.—Various methods have been suggested for converting the magnetic temperature T^* into the Kelvin temperature K. A method used by Kürti and Simon[2] and others is as follows :—

From eqn. (37) if the change in volume is negligible, as usual, we have

$$\delta Q = TdS = dU - \mathscr{H}\, d\mathscr{M}, \qquad (48)$$

provided, of course, that the process is reversible. If in addition, it is carried out at zero field ($\mathscr{H}=0$), we get

$$T = \left(\frac{\partial U}{\partial S}\right)_{\mathscr{H}=0}. \qquad (49)$$

Therefore, if we measure both U and S as a function of T^* we can calculate the corresponding Kelvin temperature T from the relation

$$T = (\partial U/\partial T^*)_{\mathscr{H}=0} \Big/ \left(\frac{\partial S}{\partial T^*}\right)_{\mathscr{H}=0} \qquad (50)$$

This is accomplished by performing three experiments.

(1) First at a fixed liquid helium temperature of above 1°K, whose actual Kelvin temperature is measured with the help of a helium vapour-pressure thermometer, the paramagnetic substance is slowly magnetised. During this reversible isothermal magnetisation the entropy increases from S_k at $T = T_i$, $\mathscr{H} = 0$ to S_i at $T = T_i$, $\mathscr{H} = \mathscr{H}_i$. This increase can be measured by determining the heat $\triangle Q$ evolved in the process since $\triangle Q = T(S_i - S_k)$. It can also be calculated with the help of the second TdS equation (See **Problem 7, p. 336**) if we remember that p and v occurring therein have to be now replaced by $\mathscr{H}$ and $-\mathscr{M}$. Thus

$$TdS = C_H\, dT + T\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{\mathscr{H}} d\mathscr{H}, \qquad (51)$$

and for the isothermal process

$$S_i - S_k = \int^{\mathscr{H}_i} \left(\frac{\partial \mathscr{M}}{\partial T}\right)_{\mathscr{H}} d\mathscr{H}, \qquad (52)$$

---

[1] Daniels and Kürti, *Proc. Roy. Soc. London*, **221**, 243, 1945; Gardner and Kürti, *Ibid*, **223**, 542, 1954.

[2] *Proc. Roy. Soc.* **149**, 161, 1935. See also Keesom, *J. de Physique*, **5**, 373, 1934.

Hence from a measurement of the susceptibility the increase in entropy $S_i - S_k$ can be calculated for any $\mathscr{H}_i$. This is shown in Fig. 26 by the line AB.

(2) Next the substance is demagnetised adiabatically from the state S_i at T_i and $\mathscr{H}_i$ to the state S_f corresponding to zero field with the resulting magnetic temperature T_f^*. As the process is isentropic (BC in Fig. 26), $S_f = S_i$. Thus we know $S_f - S_k$ for a certain value of T_f^* and $\mathscr{H} = 0$. Using different initial fields $\mathscr{H}_i$, the quantity $S_f - S_k$ can be found for different T_f^* and the results plotted (Fig. 27), from which $(\partial S_f/\partial T_f^*)_{\mathscr{H}=0}$ can be calculated.

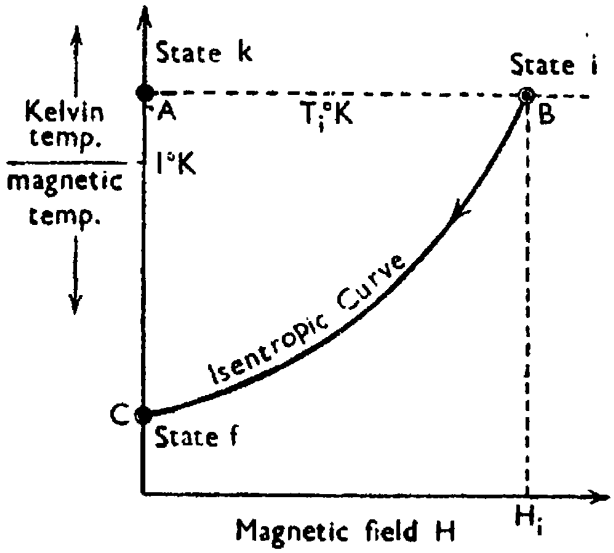

Fig. 26.—Reversible adiabatic demagnetisation

(3) In the third step the heat Q required to raise the temperature of the paramagnetic salt from T_f^* at $\mathscr{H} = 0$ to some other T^* is measured. Then from (48), since $\mathscr{H} = 0$,

$$\left(\frac{\delta Q}{dT_f^*}\right)_{H=0} = \left(\frac{dU}{dT_f^*}\right)_{H=0} = C^*_{H=0} \quad . \quad . \quad . \quad (53)$$

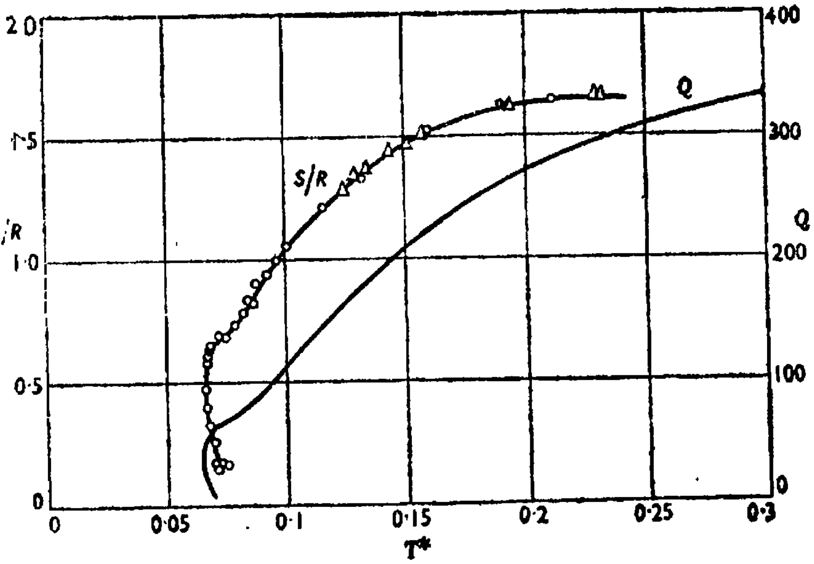

Fig. 27.—Entropy and heat content of iron ammonium alum plotted against magnetic temperature.

Three methods have been used to heat the salt: (i) heating by γ rays employed by Kürti and Simon, (ii) heating due to the small ferromagnetic hysteresis possessed by paramagnetic salts at very low temperatures employed by de Klerk, (iii) induction heating. Thus knowing δQ and dT_f^*, the quantity $(\partial U/\partial T_f^*)_{H=0}$ or C_H^* is found out. Substitution in (50) then gives the corresponding Kelvin temperature. Fig. 28 gives such a correlation curve for iron ammonium alum and such correlations have now been obtained for a number of paramagnetic salts down to 0·004°K.

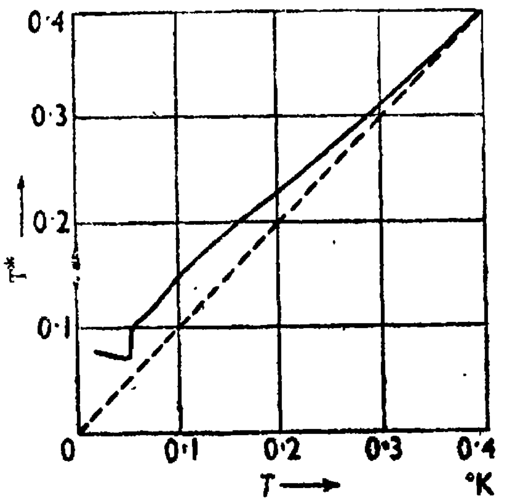

Fig. 28.—T^* as a function of T.

12·35. Temperatures below 10^{-2} °K.—The problem of attaining still lower temperatures is like that of the man who borrowed a shilling on condition that on each day he will repay half the amount of the *outstanding* debt. It is obvious that though every day his debt will diminish, if he makes payments it will never be wholly wiped off. Similarly it may be possible to reach lower temperatures by abstraction of thermal energy by any new methods which may be discovered but the mathematically absolute zero cannot theoretically be reached. But every step in the attainment of successive negative powers of ten degrees (10^{-1}, 10^{-2}, 10^{-6}) will probably call for new methods, and, for anything we know, each region may be crowded with unexpected experimental discoveries.

It appears that the method of adiabatic demagnetisation cannot take us much beyond 10^{-2} °K, but probably much lower temperatures of the order of 10^{-4} °K may be obtained by making use of "Nuclear paramagnetism." A crystal like that of Cu or Na is perfectly diamagnetic, but the nucleus of copper or sodium has been shown to possess magnetic moment of the order of 1/1836 times the ionic magnetic moment. Eqn. (44) shows that much higher values of $\mathscr{H}/T$ are required to produce appreciable cooling since the nuclear magnetic moment is so much smaller. Calculation shows that with the highest magnetic fields at present available, say 50—100 kilogauss, the starting temperature for nuclear demagnetization must be of the order of 1/100°K. It has therefore been suggested by Simon[1] and others that for producing cooling by adiabatic demagnetization of a nuclear paramagnetic, a two-stage demagnetization must be used. In the first stage an electron paramagnetic such as iron ammonium alum kept in thermal contact with a nuclear paramagnetic such as copper by means of a thermally conducting rod is adiabatically demagnetized producing a temperature of the order 1/100°K. Next the thermal contact between the two specimens is broken and the nuclear paramagnetic also demagnetized when temperatures of the order 10^{-5} °K will be produced. The greatest difficulty in these experiments is the provision of a make-and-brake thermal contact at 1/100°K. A superconducting thermal switch has been proposed which utilizes the property that the thermal conductivity of a superconductor is vanishingly small at the lowest temperatures but is increased by a magnetic field to the same value as in normal metals. Such a thermal switch has been recently[1] utilized in two-stage demagnetization experiments using electron paramagnetism in both stages, but all the difficulties for the nuclear demagnetization stage has not yet been successfully overcome. The nuclear paramagnetism has been however successfully utilized[2] for the nuclear alignment of the radioactive nucleus Co^{60} at about 0·01°K by a suitable magnetic field and the alignment effect measured from the anisotropy of the emitted γ-rays.

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[1] Kürti and Simon, *Proc. Roy. Soc.*, **149**, 152, 1935; See also Gorter, *Phys. Zeits.*, **35**, 923, 1934; Simon, Report of Strasbourg Conference, 1939, "Le Magnétisme", Vol. 3, p. 13.

Exercise.—20 grams of a paramagnetic substance obeying Curie's law is placed in a magnetic field of 10,000 œrsteds and a temperature of 3°K. What would be the temperature change if the field is reduced reversibly and adiabatically to zero. Assume the Curie constant per gram to be 0·05 and the specific heat at constant field to remain constant and equal to 0·10 cal. gm.$^{-1}$ deg.$^{-1}$ (Ans. —0·20°K.)

LIQUID AIR AND ITS USES.

12·36.—Low Temperature Technique.—The problem of storage of liquid air and other low temperature liquids, and of handling them was solved by Dewar by the discovery of the flask known after him.

The Dewar flask (shown in Fig. 29, p. 540 together with a siphon) consists of a double-walled glass vessel, the inside walls being silvered. The air is completely evacuated from the interspace between the walls which is then sealed. If some substance be now placed inside such a vessel and the top closed, it is perfectly heat-insulated, except for the small amount of heat which may creep in by conduction along the sides. The silver coatings protect the inside from radiation, and the absence of air prevents the passage of heat by conduction through the walls. If the substance be hung by thin wires inside the flask and the latter evacuated by a pump and sealed, the insulation is complete. Such an arrangement was used by Nernst in his low temperature calorimetry (§2·21). Dewar flasks are now sold in the market under the trade name "Thermos flask." They have been made entirely of metal with a long neck of some badly conducting alloy like German silver. For keeping liq. H_2 and He a further radiation shield is used.

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[1] Darby, Hatton, Rollin, Seymour and Silsbee, *Proc. Phys. Soc. London*, **64**, 861, 1951.

[2] Daniels, Grace and Robinson, *Nature*, **168**, 780, 1951; Gorter, Poppema, Steenland and Beun, *Physica*, **17**, 1050, 1951.

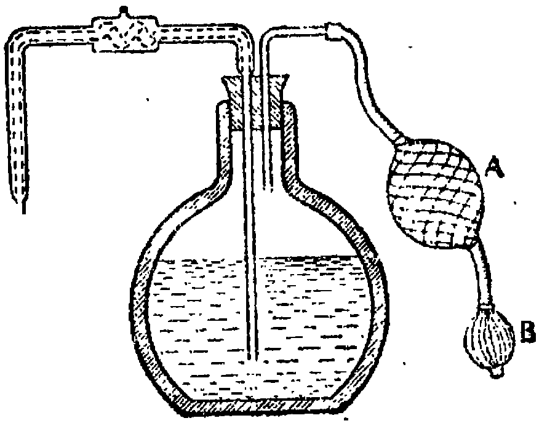

Fig. 29.—Dewar flask.

Low Temperature Siphons.—For transferring liquid air from one vessel to another, special types of siphons are used. One such siphon is shown in Fig. 29, connected to the Dewar flask. It is formed of a double-walled tube silvered inside, the space between the walls being evacuated. On the application of gentle pressure to the rubber compressors A or B, liquid air rises up the siphon and can be transferred to a second vessel.

Cryostats.—For low temperature work constant temperature baths or cryostats are necessary. The substance to be investigated is kept immersed in these baths. From table 3, p. 499 it will be easily seen that baths of liquefied gases are available in the range $-24°$ to $-218°$C, the latter being the triple point of O_2 (triple point pressure $= \cdot 2$ cm.). There are however gaps between $-218°$C and $-253°$C, which is the boiling point of H_2 at atmospheric pressure, and between the triple point of H_2 ($-259\cdot 14°$C, $p = 5\cdot 07$ cm.) and the normal boiling point of liq. He ($-268\cdot 83°$C). The first gap is bridged by a hydrogen vapour cryostat due to K. Onnes and Crommelin in which hydrogen gas is circulated at the temperature required, and the second gap can be bridged by a suitably designed He-vapour cryostat.

12·37. Use of Liquid Air and Other Liquefied Gases.—Liquid air has been, since its first manufacture in 1895, a commodity of great industrial importance. Most important cities have liquid air plants and bottles of liquid air can now be obtained in any important modern town at a comparatively small cost. We shall give some of the important uses to which liquid air has been put.

(*i*) *Production of High Vacuum.*—High vacuum can be obtained by using liquefied gases with or without charcoal. For instance, if a vessel is first filled with a less volatile gas than air, say sulphurous acid or water vapour, and be then surrounded by liquid air, all the gas inside becomes solidified and thus high vacuum is produced. If the vessel contains air, liquid hydrogen may be employed to condense it. This process is greatly assisted by charcoal which possesses the remarkable property of occluding gases at very low temperatures, and the lower its temperature the greater is the adsorption. Further also the adsorption is selective; as a general rule it may be said that the more volatile gas, the less it is adsorbed.

We shall give a numerical example. During a certain experiment a vessel containing air at a pressure of 1·7 mm. at 15°C when cooled by charcoal immersed in liquid air, gave a pressure of $4{\cdot}7\times10^{-5}$ mm. in an hour and using liquid hydrogen as the cooler the pressure was reduced to $5{\cdot}8\times10^{-6}$ mm.

(*ii*) *Analytical Uses of Air.*—Liquid air is of great use in drying and purifying gases. Water vapour and the less volatile impurities are easily removed by surrounding the gas in question (say H_2) with liquid air and for this purpose it is now a common laboratory reagent.

(*iii*) *Preparation of Gases from Liquid Air.*—Oxygen is now prepared commercially from liquid air by fractional distillation. Since the boiling point of nitrogen is −195·8°C, and that of oxygen is −182·9°C, the fraction to evaporate first will be rich in nitrogen while that evaporating last will be rich in oxygen. A few fractional distillations will suffice to separate these completely. Several rectifiers have been devised to effect this separation. In Linde's rectifier (1902), liquid air trickles down a rectifying column where it meets an upgoing stream of gas. The temperature at the top of the column is slightly below −194°C (B. P. of liquid air) while at the bottom it is −182°C (B. P. of oxygen). The rising gas at the bottom comes in contact with the down-coming liquid and thereby some oxygen of the rising gas is condensed, while some of the nitrogen in the down-coming liquid evaporates and the liquid also becomes warmer. The process continues till the liquid reaches the bottom when it contains nearly pure oxygen, while nitrogen passes off as vapour at the top. This oxygen is almost pure but the nitrogen contains about 7 % of oxygen. More efficient rectifiers have since been devised by other workers. For a description of these rectifiers and a discussion of their efficiency see M. Ruhemann, *The Separation of Gases*, Chaps. VI, VII and VIII.

We have so far treated air as a binary mixture. In reality however it contains a number of gases, the composition in percent by volume being as follows:—

Table 7.—Composition of Atmospheric air.

N_2	78·03%	H_2	1×10^{-2}
O_2	20·99	Ne	$1·5 \times 10^{-3}$
A	0·933	He	5×10^{-4}
CO_2	0·03	Kr	$1·1 \times 10^{-4}$
		Xe	$0·8 \times 10^{-5}$

Liquid air may thus be separated into two fractions—the less volatile part consisting of O_2, N_2, A, CO_2, Kr, Xe and the more volatile part consisting of He, H_2, Ne. Hence in the rectifier described above the gas going up will contain, in addition to nitrogen, He, H_2 and Ne. The nitrogen is removed by passing the gas through a dephlegmator and hydrogen may be removed by sparking with oxygen. Thus a mixture of He-Ne is obtained which is called 'technical neon' and is used commercially. Neon is removed by cooling the mixture with liquid hydrogen and in this way Meissner obtained some quantity of helium for laboratory purposes. From the liquid collecting down in the Linde rectifier A and Kr are commercially obtained by first removing oxygen by chemical means, and then A and Kr may be obtained by fractional distillation. For details of these methods see Ruhemann, *The Separation of Gases*, Chap. IX.

(iv) Calorimetric Applications.—Dewar constructed calorimeters of liquid air, oxygen, and hydrogen. He employed pure lead as the heater, and the volume of the gas evaporated by the application of this heat was measured. These calorimeters have the advantage that a large quantity of gas is formed which makes it possible to detect as little as $\frac{1}{300}$ calorie with liquid hydrogen. In this way the specific heat of lead and other substances may be investigated at low temperatures.

(v) Use of Liquid Gases in Scientific Research.—The extremely low temperatures which are now available to us by the use of liquid air and liquid hydrogen and helium have opened for the investigator a new and vast field for research. This has made a liquid air plant essential for every modern laboratory. Most of the important properties of matter have been investigated at low temperatures and have yielded results of far-reaching importance.

(*vi*) *Industrial Uses of Liquid Gases.*—Liquid air is used commercially for the preparation of oxygen as has already been discussed. For submarines and aeroplanes it may be found useful to store liquid air or liquid oxygen for respiration but the low thermodynamic efficiency inherent in the Linde machine prevents the use of liquid air in a heat engine on any large scale, though mixtures of liquid O_2 and H_2 have been successfully used recently as a highly efficient light-weight fuel for jet-propelled aero-engines. Liquid oxygen is employed on a small scale for preparing explosives, for when mixed with powdered charcoal and detonated, it explodes with great violence. It is quite safe if it misfires since it evaporates quickly. O_2 and H_2 are now used for welding and other metallurgical industries on a huge scale. Hydrogen purified from coke oven gas by rectification is now used for hydrogenation of oils, while hydrogen from water gas and nitrogen from air are used on a huge scale for the manufacture of artificial ammonia fertiliser.

PROBLEMS

1. Find the minimum amount of work needed to extract 100 calories of heat from a body at the temperature of —5°C when the temperature of the surroundings is 40°C.

2. Show that the 'free expansion' or Joule coefficient $\eta=(\partial T/\partial p)_u$ and the Joule-Thomson coefficient μ are connected by the relation

$$\eta\left\{C_p-\left(\frac{\partial(pV)}{\partial T}\right)_p\right\}=\mu C_p+\left(\frac{\partial(pV)}{\partial p}\right)_T.$$

3. Saturated water at one atmospheric pressure undergoes throttling expansion to a pressure of $\frac{1}{2}$ atmos. Calculate the quality of the resulting mixture (Use Steam Tables).

Books Recommended

1. L. C. Jackson, *Low Temperature Physics* (1950), Methuen & Co. Ltd., London.

2. M. and B. Ruhemann, *Low Temperature Physics* (1937), Cambridge University Press.

3. Burton, Smith and Wilhelm, *Phenomena at the Temperature of Liquid Helium* (1940), Reinhold Publishing Corporation, New York.

4. W. H. Keesom, *Helium* (1942), Elsevier, Amsterdam.

5. M. Ruhemann, *The Separation of Gases*, (1940), Clarendon Press, Oxford.

6. Glazebrook—*A Dictionary of Applied Physics*, Vol. I, articles on 'Refrigeration' and 'Liquefaction'.

7. B. F. Dodge, *Chemical Engineering Thermodynamics* (1944), McGraw-Hill Book Co., New York.

8. *Handbuch der Physik*, Vol. XI, Chap. VII.

9. *Handbuch der Experimental-Physik*, Vol. IX, Part I, pp. 47—186.

10. Robinson and Dickson, *Applied Thermodynamics* (1947), Pitman & Sons, London.

11. C. F. Squire, *Low Temperature Physics* (1953), McGraw-Hill Book Co. New York.

12. C. J. Gorter, *Progress in Low Temperature Physics* (1955), North-Holland Publishing Co. Amsterdam.

13. *Low Temperature Physics*—four lectures by Simon, Kürti, Allen, Mendelssohn (1952), Pergamon Press Ltd., London.

14. H. G. B. Casimir, *Magnetism and Very Low Temperatures* (1940), Cambridge University Press.

CHAPTER XIII

THERMAL EXPANSION

13·1. The size of all material bodies changes on being heated. In the majority of cases, the size increases with rise in temperature, the important exceptions being water and some aqueous solutions in the range 0° to 4°C., the iodide of silver (resolidified) below 142°C and some nickel-steel alloys. We shall first consider the expansion of solids.

EXPANSION OF SOLIDS

13·2. The cubical expansion of solids is somewhat difficult to measure directly (a method is given in §13·20), and is generally calculated from the linear expansion. Hence experiments on the expansion of solids generally consist in measuring the linear expansion of bars or rods of the solid. For isotropic bodies whose properties are the same in all directions, the expansion is also the same in all directions. To this class belong amorphous solids (*e.g.*, glass) and regular systems of crystals (*e.g.*, rock salt). Metals may also be included because though they are composed of a very large number of small crystals, these crystals are oriented at random and the *average* properties are independent of direction. In anisotropic bodies which include crystals, the expansion is different in different directions and may be even of different sign. We shall first consider isotropic bodies while anisotropic bodies will be considered later.

Isotropic Solids

13·3. Linear Expansion.—If a bar of length l_0 at 0°C has a length l_t when raised to t°C, l_t is given by

$$l_t = l_0\,(1+\int a\,dt). \qquad . \quad . \quad . \quad . \quad (1)$$

If l_t is expressed as a linear function of t of the form

$$l_t = l_0\,(1+\lambda t), \qquad . \quad . \quad . \quad . \quad (2)$$

λ is called the mean linear coefficient between the temperatures 0° and t°C and is a very small quantity. When the difference between the initial and final temperatures is small, λ differs very little from a.

The mean coefficient of expansion, λ is found to vary with temperature. Thus its value λ_t at any temperature is given by

$$\lambda_t = \lambda_0 + \lambda_1 t + \lambda_2 t^2 + \dots, \qquad \dots \quad (3)$$

in which the constants λ_0, λ_1 and λ_2 are in decreasing order of magnitude.

From (1), (2) and (3) we get

$$\begin{aligned} l_t &= l_0(1+\int \alpha dt) = l_0(1+\lambda t) \\ &= l_0\{1+t(\lambda_0+\lambda_1 t+\lambda_2 t^2)\} \\ &= l_0\{1+\int(\lambda_0+2\lambda_1 t+3\lambda_2 t^2)dt\} \\ \therefore \alpha_t &= \lambda_0+2\lambda_1 t+3\lambda_2 t^2, \qquad \dots \quad (4) \end{aligned}$$

Equations (3) and (4) give the relations between the variations of true and mean coefficients of expansion with temperature. In most cases both the constants λ_1 and λ_2 are positive, the value of the coefficient of expansion increasing with temperature.

13·4. Earlier Measurements of Linear Expansion.—The linear expansion of solids is very small : a bar of iron one metre long when heated from 0°C to 100°C, increases in length by 1·2 mm. To measure such small changes in length accurately, special devices are necessary. The increase of length can be measured with the help of optical levers, travelling microscopes, interferometers and also by photographing the X-ray diffraction patterns at different temperatures.

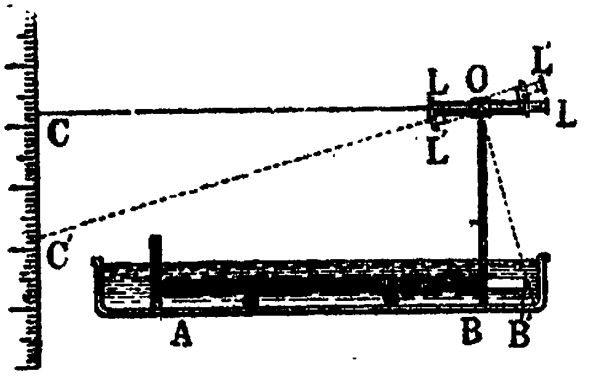

Fig. 1.—Apparatus of Laplace and Lavoisier.

The first accurate determination of linear coefficient of expansion of solid bodies was made in 1782 by Lavoisier and Laplace.[1] In the instrument used by them the change in the length was converted into a change in the angle by means of a lever arrangement and the rotation was measured by using a scale and a mirror or a telescope. The principle of this apparatus is indicated in Fig. 1. One end A of the experimental bar AB is fixed while the other end B pushes against a vertical lever OB attached at right angles to the axis of a telescope LL, which is itself pivoted at O and is focussed on a distant vertical scale CC′. The bar AB is first placed in melting ice and the scale division C seen through the telescope is noted. Next the bar is enclosed in a hot-water bath. The rod AB expands to B′ thereby tilting the telescope LOL to the position L′OL′ and the scale division C′ is now seen through the telescope. The expansion BB′ is equal to OB′×OC′/OC.

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[1] *Bot. Traite de Physique*, Tom. 1, Paris, 1816.

Paschen employed a combination of the micrometer screw and the lever. The expansion was multiplied in the ratio 1 : 5 by the lever and this magnified change in length was measured by the micrometer screw.

In 1785 Roy and Ramsden devised a method in which an object-glass fixed at one end of the experimental bar and a micrometer eyepiece fixed at the end of a similar bar placed by the side of the experimental bar were used to measure the small increment of length with the rise of temperature. The experimental bar was five feet long and was placed in a trough between two similar bars placed parallel to and on the opposite sides of the experimental bar. The image of two vertical wires fixed near the end of one of the outer bars formed by the object-glass fixed at the end of the experimental bar was seen through the micrometer eye-piece fixed at the end of the third bar, the centre of a cross hair in the eye-piece being brought into coincidence with the centre of the image. When the experimental bar was heated to 100°C by boiling water, the object glass shifted and by shifting the micrometer eye-piece the image of the wires was again brought into coincidence with the cross hair as before. From this shift of the micrometer eyepiece, that of the object glass could be determined by noting previously how much shift of the image in the micrometer eyepiece was equivalent to a shift in the object glass through a distance equal to the distance between the two vertical wires. During the experiment, the two outer bars were kept covered with melting ice and so their length remained constant.

13·5. Standard Methods.—At the present time the standard methods employed for measuring linear expansion are :—

(1) Comparator Method, (2) Henning's Tube Method, (3) Interferometric Method and (4) X-ray method. Methods (1), (3) and (4) are direct while method (2) is indirect.

13·6. Comparator Method.—In this method the substance in the form of a bar about a metre long is placed horizontally in a trough by the side of a standard metre placed parallel to the former and kept at a constant temperature. The experimental bar is provided with a fine mark at each end. Two microscopes provided with micrometer eyepieces are fixed vertically in rigid horizontal supports projecting out from stout pillars, the distance between the microscopes being about one metre. First the fine marks on the bar are viewed through the two microscopes and their positions are noted in the micrometer. The standard metre is then brought below the microscopes and the two extreme marks of graduation are viewed through the microscopes. From the change in the micrometer reading the length of the bar at the lower temperature is obtained. The experimental bar is then heated by keeping it immersed in a bath at constant temperature and the marks are again viewed through the micrometer eyepiece. The increase in length is determined from the change in the micrometer reading. For measurements at low temperatures, the experimental rod is placed in a tube which is immersed in a suitable liquid bath[1] (e.g., liquid air).

For measuring the expansion over a wide range e.g., from —150°C to 650°C, the above method can be modified.[2] Instead of

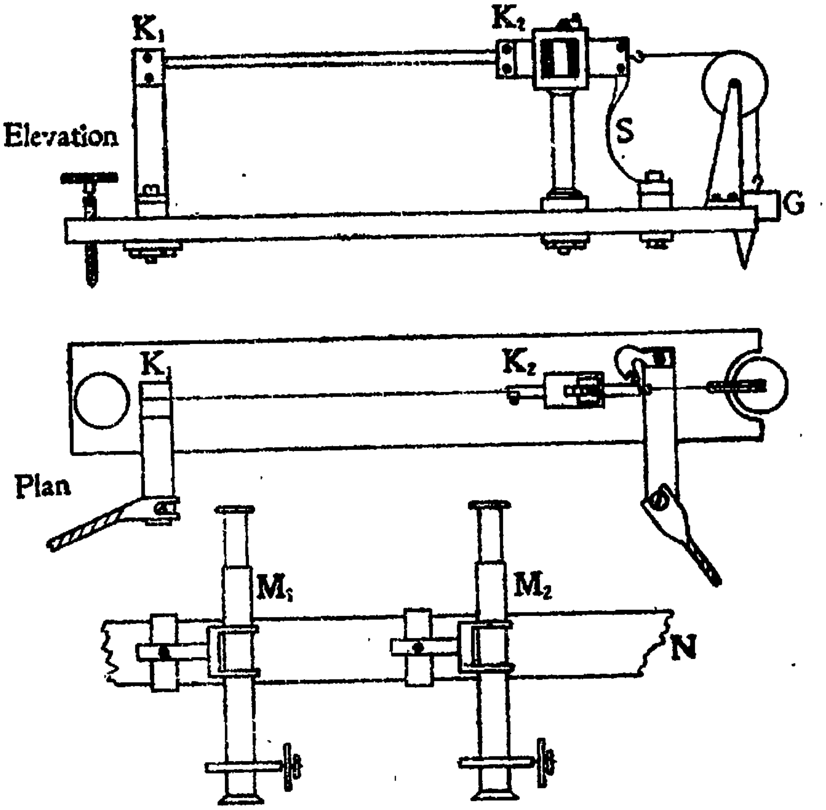

Fig. 2.—Comparator method of measuring linear expansion.

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[1] Scheel and Heuse, *Verh. d. D. Phys. Ges.*, **9**, 449, 1907.

[2] Gray, *Chem. and Metallurg. Eng.*, **21**, 307, 1919.

putting fine marks at the ends of the bar a lightly stretched vertical fine wire can be attached at each end of the bar and the distances between the wires at the lower and higher temperatures can be measured with a comparator.

If the expansion at a still higher temperature is required the method devised by Holborn and Valentiner[1] is suitable. The material is taken in the form of a thin strip about 25 cm. long, 1 cm. wide and 0·2 mm. thick and clamped between two clamps K_1 and K_2 (Fig. 2, p. 548), K_1 being fixed while K_2 can be moved by means of the pulley and weight G. The positions of two marks at its two ends are noted through two microscopes M_1, M_2 fixed on invar stand N. The strip is then heated by passing electric current through it and the temperature is measured with an optical pyrometer. The change in its length is measured with the help of the two microscopes.

13·7. Henning's Tube Method[2] of Measuring Relative Expansion.

—In this method, the experimental and the comparison bodies are together brought to the same temperature and the differential change of their lengths is measured. The comparison body is so chosen that its expansion in the temperature region is accurately known and, if possible, is also very small. Fused silica serves this purpose well. Inside a long vertical tube made of some well-defined glass (fused silica, Jena glass), there is a ground point, molten and drawn out of the same glass at its lower end. Upon this point rests the experimental rod R (Fig. 3), about 50 cm. long and having both of its end faces ground plane. Upon the upper surface of R rests a pointed end of another glass rod S made of the same glass as the outer wider tube. To the upper end of this rod as well as of the

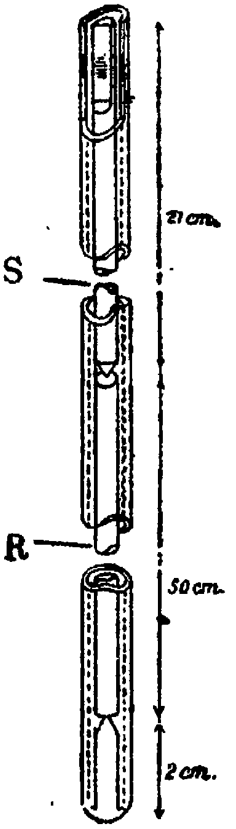

Fig. 3.—Henning's Apparatus.

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[1] *Ann. d. Phys.*, **22**, 12, 1907.

[2] *Ann. d. Physik*, **22**, 631, 1907; Holborn and Henning, *Zeits. f. Instrkde.*, **32**, 122, 1912; Simon and Bergmann, *Zeits. f. Phys. Chem.*, B, **8**, 255, 1930.

outer tube, are attached end-pieces carrying scales. The whole tube up to half of the height of the rod S is immersed in a hot or cold bath and the relative shift of the end-pieces is measured with a microscope provided with a micrometer eye-piece. The shift gives the relative expansion of the experimental rod against a glass tube of equal length. This is so on the assumption that the temperature of the rod and of the outer tube is the same at the same height. For high[1] and low[2] temperatures suitable baths may be employed.

13·8. Fizeau's Interference Method.—Fizeau[3] devised a method in which a small change in length produces a shift in Newton's rings and by measuring the shift, very small change in length can be measured. In his original experiment, Fizeau used the substance B (Fig. 4) in the form of a slab about 1 cm. thick with two of its opposite plane faces parallel and polished. It was placed with one of these faces horizontal on a metal plate A supported by three levelling screws S,S. These screws projected upward through the metal plate a little beyond the upper face of the slab B. A convex

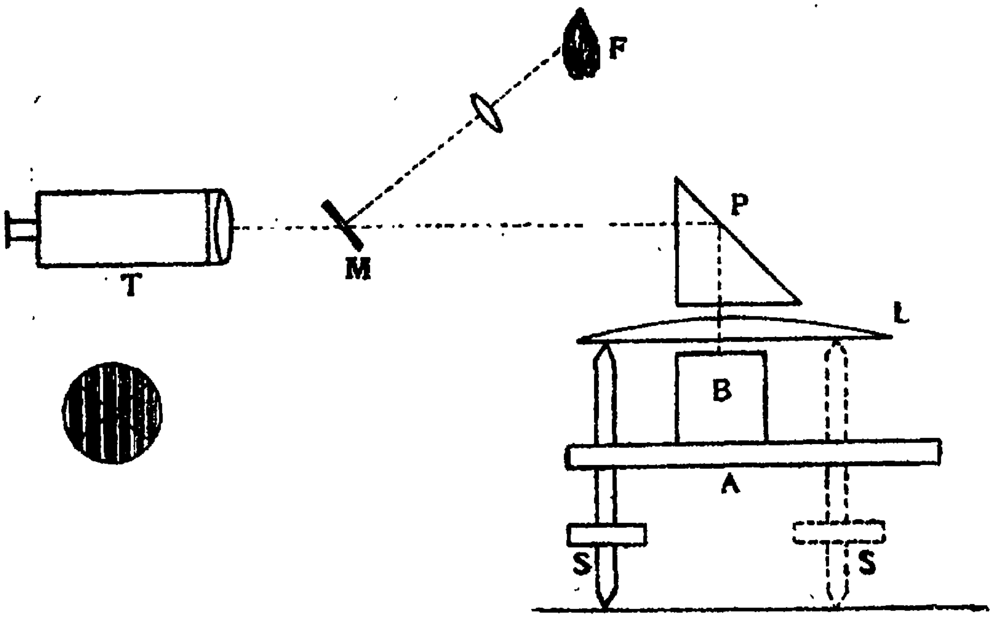

Fig. 4.—Fizeau's interference method for measuring linear expansion.

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[1] Holborn and Day, *Ann. d. Physik*, **2**, 505, 1900; **4**, 104, 1901. Holborn and Valentiner, *Ann. d. Physik*, **22**, 1, 1907.

[2] Grüneisen and Goens, *Zeits. f. Physik*, **29**, 141. 1924, Lindemann, *Phys. Zeits.*, **12**, 1197, 1911.

[3] *Ann. Chim. Phys.* (4), **2**, 143, 1864; **8**, 335, 1866; *Pogg. Ann.*, **123**, 515, 1864; **128**, 571, 1866.

lens L having the lower surface of very large radius of curvature was placed on these screws so that a thin film of air lay between this surface of the lens and the upper polished surface of the slab. With the help of a mirror M and a right-angled prism P placed above the lens, horizontal rays of light from a sodium flame F were sent in a vertical direction to illuminate the air film and the rays reflected repeatedly at the surface of the slab and the lower surface of the lens proceeded vertically upwards and were again reflected by the right-angled prism. When these rays were received by a horizontal telescope T, Newton's rings could be seen through the telescope.

The difference in the thickness of the film at two successive bright rings is $\lambda/2$, where λ is the wave length of the light used. Hence when the thickness of the film changed due to expansion of the slab and of the three screws supporting the lens the rings appeared to pass across a mark in the lens. Since one-tenth of the distance between successive bright rings could be measured the change in length of the order of $\lambda/20$, i.e., about 0·00002944 mm. could be measured.

When the arrangement producing the thin air film was enclosed in a heating chamber the thickness of the film changed and the shift of a bright ring from its original position was noted. These observations gave the difference in the expansion of the projecting portion of the supporting screw and of the slab along its thickness. If the former expansion were known the latter could be found out. In order to find the expansion of the screws, the slab was removed and interference rings were produced by reflections at the lower surface of the lens and the polished surface of the metal plate through which the screws projected.

Abbe[1] and Pulfrich[2] improved Fizeau's apparatus by replacing the screws by quartz ring as shown in Fig. 5, p. 552. The specimen of which the expansion is to be measured is taken in the form of a cylinder about 1 cm. long with both its faces polished and plane parallel. It is placed on a quartz plate G and is surrounded by a quartz ring R cut so as to have its axis parallel to the optic axis in the walls of the ring. The ring has three projecting portions on which a quartz plate D, having both of its plane faces polished, and parallel to each other, is placed. The total height of the ring is slightly greater than the length of the cylindrical specimen and the ring is so cut that the lower face of the quartz plate D and the upper face of the specimen encloses a wedge shaped air film, the angle of the wedge being very small. This arrangement is placed in a container immersed in suitable bath or heater for investigations at low or high temperatures.[1] The air film is illuminated normally as shown in Fig. 6. Light from a Geissler tube containing mercury and hydrogen or mercury and helium is focussed on the inclined face of a right-angled prism placed at the focal plane of an object glass. The rays reflected at the prism surface are converted into a parallel beam by the object glass and these are deviated downwards by the two prisms P, P. After suffering reflection at the two surfaces of the air film they travel through the prism and the fringe systems for different wave-lengths are formed at different heights in the focal plane of the object glass. Thus the fringe system due to a red line consists of a row of short parallel vertical fringes and those due to a green line form a similar row below the former one and separated from it. By turning a screw any of these rows can be brought in the field of view of the micrometer eyepiece through which the fringes are viewed. The lower surface of the upper quartz plate D is provided with a mark of reference and the number of the fringes crossing this reference mark due to the change in thickness of the air film with the rise of temperature of the system containing the specimen can be measured with the help of the micrometer eyepiece. Actually the numbers of fringes of

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[1] *Wied. Ann.*, **38**, 453, 1889.

[2] *Zeits. f. Instrkde.*, **13**, 364, 1893.

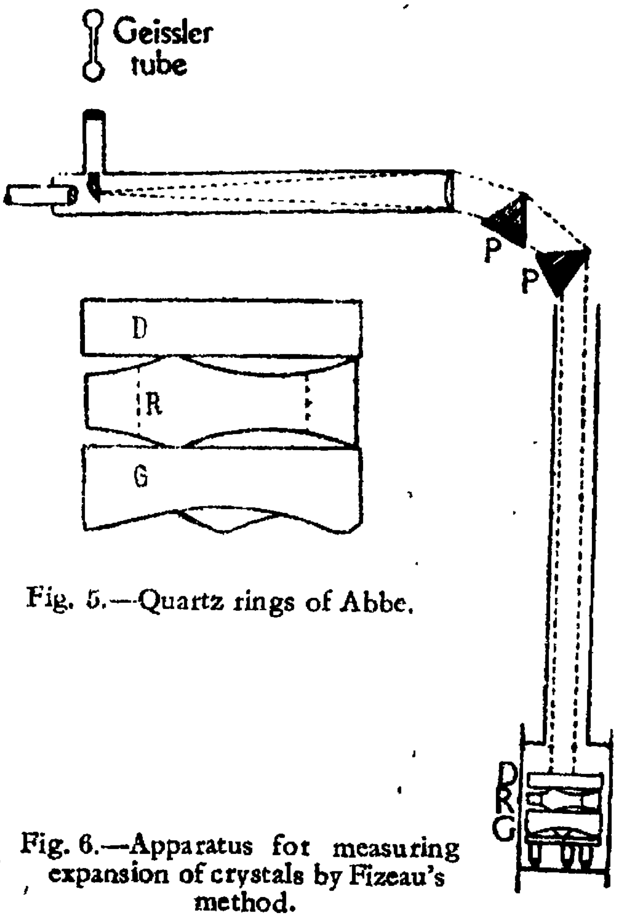

Fig. 5.—Quartz rings of Abbe.

Fig. 6.—Apparatus for measuring expansion of crystals by Fizeau's method.

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[1] Scheel, *Ann. d. Physik*, **9**, 887, 1902.

wavelengths λ_1, λ_2, λ_3 etc. crossing the reference mark are $x_1+\xi_1$, $x_2+\xi_2$, $x_3+\xi_3$, etc., where x_1, x_2, x_3 etc., are whole numbers and ξ_1, ξ_2, ξ_3, etc. are fractions and only these fractions ξ_1, ξ_2, ξ_3, etc., are measured accurately with the help of the micrometer. The values of x_1, x_2, x_3, etc., are derived in the following way :—

The difference of path at the successive bright fringes being $\lambda_1/2$, the total change dl in thickness of the air film at the mark is $(\lambda_1/2)(x_1+\xi_1)$ if the number of fringes of wave length λ_1 passing through the mark due to expansion be $x_1+\xi_1$. The same change in thickness causes $x_2+\xi_2$ fringes of wave-length λ_2 to cross the mark.

Hence $$dl = \frac{\lambda_1}{2}(x_1+\xi_1) = \frac{\lambda_2}{2}(x_2+\xi_2) = \frac{\lambda_3}{2}(x_3+\xi_2) = \ldots\ldots,$$

or $$\frac{\lambda_2}{\lambda_1}x_2 - x_1 = \xi_1 - \frac{\lambda_2}{\lambda_1}\xi_2 \text{ etc.,} \qquad (5)$$

In order to calculate x_2 we give different whole number values to x_1 in (5) and find out for which value of x_1, x_2 becomes a whole number with the values of ξ_1 and ξ_2 determined experimentally. A knowledge of the approximate expansion of the specimen helps in determining the order of magnitude of x_2. For details of calculation see *Handbuch der Physik*, Vol. 10, p. 88.

13·9. Priest's Fringe Width Dilatometer.

—In the last method the change in length was found from observations on displacement of the fringes. Priest[1] devised a dilatometer in which changes in length can be obtained from the change in width of the interference fringes. The apparatus is indicated in Fig. 7.

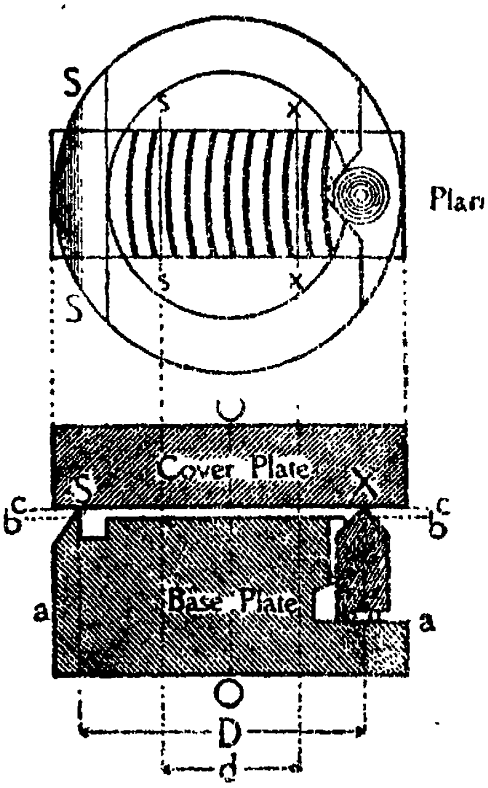

Fig. 7.—Priest's Fringe Width Dilatometer.

The air film is enclosed between the lower surface of the cover plate and the upper surface of the base plate, both of which are optically plane and enclose a wedge-shaped space (0·1 to 0·3 mm. thick). On looking down in the direction OO, a system of interference fringes will be seen (as shown in the plan) appearing to lie in the plane *bb* so that the fringes and the reference lines *ss* and *xx* on the mirror can be simultaneously focussed. The sample ends at the top in a fine point X upon which rests the cover plate. The sample, on expanding tilts the cover plate and thereby changes the thickness of the air film and consequently the width of the fringes. The number of fringes between the lines *ss* and *xx* are observed both initially and finally, and from this the expansion can be calculated.

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[1] *Bull. Bur. of Stand.*, 15. 669, 1920.

The calculations can be readily made. If D is the perpendicular distance from X to knife-edge SS, $\triangle$ the relative expansion of the sample with respect to a piece of equal height made from the material composing the base plate, then the change ϕ in the angle between the planes *bb* and *cc* measured in radians is given by

$$\phi = \frac{\Delta}{D}. \qquad \qquad (6)$$

since ϕ is small.

Again if the number of fringes between the marks *ss* and *xx* changes by $x+\xi$ and d denotes the perpendicular distance between *ss* and *xx* and λ the wave-length of the light employed, then the change in angle is also given by

$$\phi = \frac{2}{\lambda}\cdot\frac{x+\xi}{2}. \qquad \qquad (7)$$

Combining (6) and (7) we get

$$\triangle = \frac{\lambda D}{2d}(x+\xi). \qquad \qquad (8)$$

Knowing $\triangle$, the coefficient of expansion can be calculated.

13·10. Recording Interferometric Dilatometer.—

The interferometric dilatometer designed recently by Nix and MacNair[1], incorporates in itself an interferometric arrangement for the measurement of the change of temperature as well. The section view of the arrangement is shown in Fig. 8 at S while the plan view of the fringes is shown at P.

Three small pyramids of the material each of height about 4 mm. rest on a silica disc of diameter about 27 mm. The upper surface of the disc is optically flat and polished, but only a small portion of the lower surface near the edge is polished.

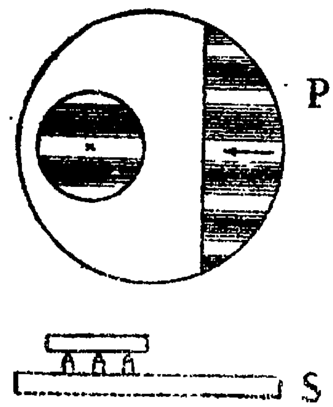

Fig.8.—Interferometric Dilatometer of Nix and MacNair.

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[1] *Rev. Sci. Inst.*, **12**, 66, 1941.

These two surfaces form a wedge which, when illuminated normally by a parallel beam of monochromatic light, forms a system of fringes. When the temperature of this plate changes, some fringes will pass through a fiduciary mark. From a knowledge of the temperature dependence of the refractive index of silica and the thickness of the wedge, it is possible to calculate the temperature difference corresponding to a definite number of fringes crossing the fiduciary mark. The upper silica plate is about 10 mm. in diameter and its upper and lower faces are optically flat and polished. These form a wedge having an angle of 15° so that no disturbing interference pattern is formed by reflection of the normally incident light at the two surfaces. The lengths of the three small pyramids of the material to be investigated are so adjusted that when the upper plate is placed on them, the lower surface of the upper plate and the upper surface of the lower plate form a wedge of a very small angle, and only 2 fringes are produced when the wedge is illuminated normally by monochromatic light in the visible region. This fringe system and that produced by the silica thermometer are formed side by side as shown in the plan view of the fringes at P in the figure. By using a half-silvered mirror inclined at an angle of 45° with the incident rays the fringe systems can be photographed with a camera.

13·11. Discussion of Results.—Table 1 below gives the mean coefficient of expansion λ of several substances between 0 and 100°C.

Table 1.—*Coefficient of Linear Expansion of Substances.*

Substance.	$\lambda \times 10^6$ in °C.$^{-1}$	Substance.	$\lambda \times 10^6$ in °C.$^{-1}$
Aluminium ..	23·8	Nickel ..	13·0
Copper ..	16·66	Platinum ..	8·86
Cadmium ..	31·59	Palladium ..	11·04
Chromium ..	8·4	Silver ..	19·68
Lead ..	28·0	Tungsten ..	4·50
Magnesium ..	26·0		
Manganese ..	22·8	Quartz glass ..	0·51
Molybdenum ..	5·20	Jena glass ..	8·08

But as already mentioned in §13·3 these values change appreciably, if the final temperature is different from 100°C. The mean coefficient λ is a function of the temperature. As the final temperature is lowered, the coefficient decreases. Grüneisen[1] has found the value of the quantity $\lambda_t = \frac{1}{l_0}\frac{dl}{dt}$ for very low temperatures and has developed an important law connecting the coefficient of expansion and the specific heat. Grüneisen's law states that *for a metal the ratio of the coefficient of linear expansion to its specific heat at constant pressure is constant at all temperatures.*

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[1] *Ann. d. Physik*, **26**, 211, 1908.

The law can be tested by determining the values of true coefficients of expansion and specific heat of a substance at different temperatures. Several investigators have shown that the law holds good in the case of a large number of metals. The results obtained by Nix and MacNair[1] with their improved interferometric dilatometer for Cu, Al, Au, Ni and Fe show that the law holds good very accurately in the temperature-ranges from $-185{\cdot}5$°C to $500{\cdot}1$°C in the case of Cu, from -187°C to $729{\cdot}8$°C for Au and from -191°C to $393{\cdot}8$°C for Al. In the case of Ni and Fe, however, there are deviations in the high temperature regions. The results for gold and iron are reproduced in Fig. 9 and Fig. 10 respectively. Attempts have been made to develop the theory of the solid state and to deduce Grüneisen's law theoretically. For details see Seitz, *The Modern Theory of Solids* (1940), Chap. X.

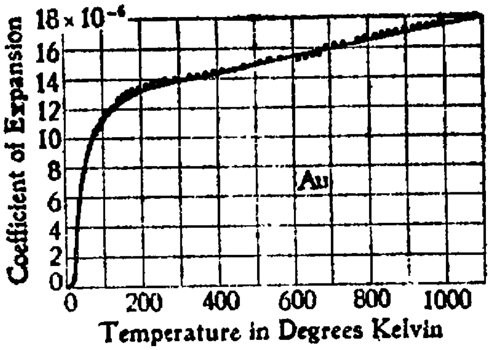

Fig. 9.—Thermal expansion of gold.

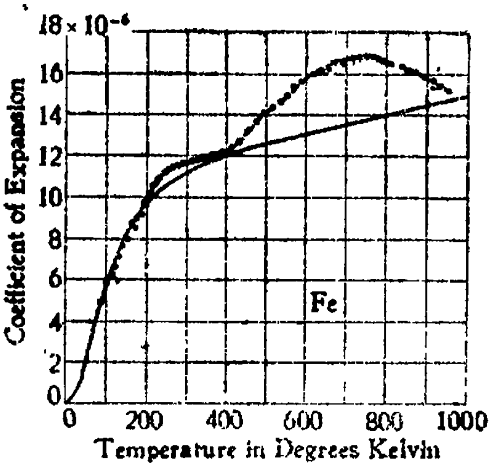

Fig. 10.—Thermal expansion of iron.

13·12. X-ray Method.—As mentioned in §13·2, some crystals belonging to the cubic system and metals can be regarded as isotropic solids. In the case of single crystals of such substances a parallel beam of X-rays is reflected by a set of planes of indices h, k, l when the glancing angle θ made by the rays with the plane satisfies the Bragg relation

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[1] *Phys. Rev.*, **60**, 597, 1941.

$$2d_{hkl} \sin \theta = n\lambda, \quad . \quad . \quad . \quad . \quad (9)$$

where d_{hkl} is the spacing of the planes, i.e., perpendicular distance between the adjacent members of the set of planes, λ is the wavelength of X-rays used and n is an integer. These spacings are determined at two different temperatures t°C and t_0°C with a Bragg spectrometer in the case of single crystals or with the help of a Debye-Scherrer camera in the case of a crystal powder or a fine metallic wire which consists of small crystals oriented at random. If d_t and d_0 be the spacings at temperatures t°C and t_0°C and θ and θ_0 be the corresponding Bragg angles

$$\frac{d_t}{d_0} = \frac{\sin \theta_0}{\sin \theta} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The mean coefficient of expansion

$$= \frac{d_t - d_0}{d_0\,(t - t_0)} = \frac{\sin \theta_0 - \sin \theta}{(t - t_0) \sin \theta}. \quad . \quad . \quad . \quad (11)$$

In the case of a Debye-Scherrer pattern the reflections from different planes take place from crystals oriented at the proper Bragg angles in all azimuths around the incident beam, and when these reflected X-rays are photographed on a plane photographic film, rings around the central spot due to the incident beam are observed. The diameter of the ring diminishes if the spacing of the plane is increased due to rise in temperature. The patterns obtained in the case of platinum wire at two different temperatures are reproduced in Fig. 11.

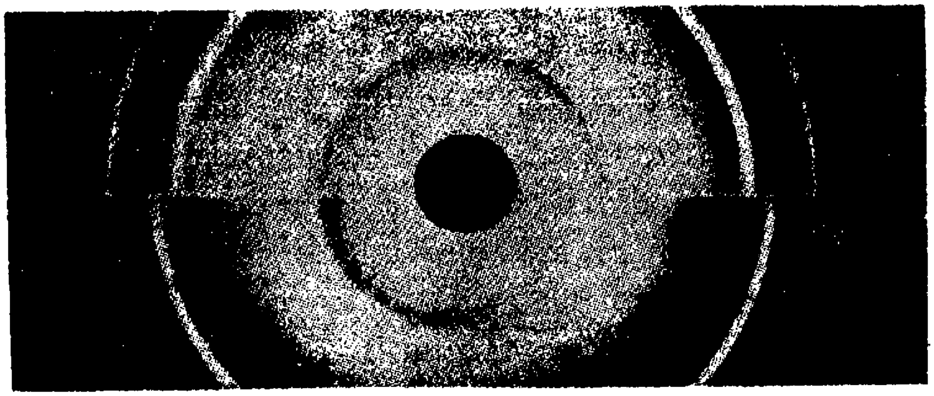

Fig. 11.—Debye-Scherrer patterns of platinum wire at two temperatures.

13·13. Expansion of Silica Glass, Invar.—Silica glass (quartz which has been fused and resolidified into the non-crystalline form) is now commonly employed for the construction of thermometers. Several experimenters have investigated its expansion and a summary of these results has been given by Kaye.[1] The expansion of silica is very small ($\lambda = 0 \cdot 5 \times 10^{-6}$) and is very conveniently determined by Fizeau's method. Hence vessels made of this material can be heated without any fear of breaking. The curve connecting the coefficient of expansion and temperature is a straight line between the room temperature and 1000°C, but at both limits it bends. The coefficient is negative below −80°C.

Invar is another special substance, being an alloy of nickel and steel. Its coefficient of expansion at ordinary temperatures is almost zero and hence it is generally employed for making secondary standards of length, and in the manufacture of precision clocks and watches.

13·14. Surface and Volume Expansion.—The change in area and volume can be easily calculated from a knowledge of the coefficient of linear expansion. A rectangle of sides l and b will, on being heated, have sides of lengths $l(1+\lambda t)$ and $b(1+\lambda t)$, and its area will become $lb(1+\lambda t)^2$. If the initial and final areas be A_0 and A we have

$$A = A_0(1+2\lambda t) \text{ approx.} \qquad \qquad (12)$$

since λ is small. Thus the coefficient of surface expansion is 2λ. Similarly the coefficient of volume expansion can be shown to be 3λ.

ANISOTROPIC BODIES

13·15. It was first observed by Mitscherlich[2] that the angles between the cleavage faces of a crystal of Iceland spar change when the crystal is heated. He gave the correct explanation of the phenomenon, *viz.*, that the expansion of the crystal is different in different directions and this is the cause of the change in angle. Such substances are called anisotropic or non-isotropic. Most crystals belong to this class.

For most crystals, however, there can be found three mutually perpendicular directions, such that, if a cube is cut out of the crystal with its sides parallel to these directions and heated, the angles will remain right angles though the sides will become unequal. These directions are called the *principal axes of dilatation* and the coefficients of expansion in those directions are called the *principal*

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[1] *Phil. Mag.*, **115**, 723, 1910.

[2] *Pogg. Ann.*, **41**, 243, 448, 1867.

coefficients of expansion. Denote these by λ_x, λ_y, λ_z. Such a cube of sides l_0 will, on being heated to t°C, become a rectangular solid whose edges will be given by

$$l_x = l_0(1+\lambda_x t);\ l_y = l_0(1+\lambda_y t);\ l_z = l_0(1+\lambda_z t), \quad . \quad . \quad (13)$$

and volume by

$$l_x\, l_y\, l_z = l_0^3\,[1+(\lambda_x+\lambda_y+\lambda_z)t]. \quad . \quad . \quad . \quad . \quad (14)$$

The volume coefficient of expansion is thus $\lambda_x+\lambda_y+\lambda_z$. In the case of crystals which possess an axis of symmetry, there are only two principal coefficients—one along that axis and the other perpendicular to it.

The coefficient of expansion in any direction can be easily calculated in terms of the principal coefficients. It can be shown[1] that the coefficient of expansion of a line whose direction cosines relative to the principal axes of dilatation are l, m, n is given by $l^2\alpha_1+m^2\alpha_2+n^2\alpha_3$ where α_1, α_2, α_3 are the principal coefficients.

13·16. Experimental Methods and Results.—Crystals are best investigated by the interference method. Fizeau's apparatus, or better still, Pulfrich's modification of Fizeau's apparatus, may be employed. The crystal is cut in the manner desired, into a plate with parallel faces from 1 to 10 mm. thick, and is placed between the glass plate and the metal disc. The details of these experiments have already been given.

When the expansion along the various axes of different crystals is investigated very interesting results are obtained. In the hexagonal system, for optically negative crystals, the expansion along the axis is always greater than that along an axis at right angles to it; while for optically positive crystals the reverse is the case. Thus for Iceland spar there is expansion parallel to the axis while contraction perpendicular to it. The contraction is always much less than the expansion so that the volume coefficient remains positive.

13·17. Results of X-ray Investigations.—As explained in §13·12, the spacings of different sets of parallel atomic planes of a crystal can be determined by measuring the glancing angles which a parallel beam of X-rays of known wavelength makes with these planes when Bragg reflection takes place. If d_t and d_0 be the values of the spacings of these planes at $t°$ and 0° C, the value of α, the coefficient of expansion, is given by

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[1] For a proof see Glazebrook, *A Dictionary of Applied Physics*, Vol. I, p. 876.

$$d_t = d_0(1+\alpha t). \quad . \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

In the case of isotropic crystals such as rock-salt and of metallic wires in which the small crystals are oriented at random the value of α determined by measuring the spacings of any set of atomic planes is the same as that obtained from any other set of planes. In the case of anisotropic crystals, however, the coefficients of expansion along the three adjacent edges of the unit cell of the lattice are not the same. Hence the ratio of the increase in the spacing to the original spacing is different for different parallel sets of atomic planes in such cases. Graphite is a typical example of such a case. This crystal belongs to hexagonal system and Nelson and Riley[1] have observed that the spacing of planes (0006, 0004) perpendicular to the hexagonal axis increases with temperature rapidly as is indicated by the gradual shifting of the 0006 doublet in Fig. 12 (Plate I) towards the low-angle end of the film with rise of temperature. The spacings of the sets of planes ($11\bar{2}0$, $20\bar{2}0$) parallel to the hexagonal axis however remain almost constant with the rise of temperature. For other planes, the expansion increases as the direction of expansion (viz., normal to the atomic planes) becomes more nearly parallel to the hexagonal axis ($11\bar{2}2$, $11\bar{2}4$, $10\bar{1}5$).

For Zn[2], Bi[3] and quartz[4] crystals which also are hexagonal, the expansion in a direction parallel to the hexagonal axis has been found to be different from that in a direction perpendicular to it. For bismuth Jay observed that the coefficient of expansion is constant upto 75°C, then it suddenly rises and again remains constant upto 240°C, showing the existence of an allotropic modification at 75°C. Similarly quartz showed a discontinuity at 579°C.

Most of the workers have found that the coefficients of expansion obtained by the X-ray method closely agree with the results found from ordinary macroscopic observations made upon single crystals of these substances. In other words the expansion law of the lattice is the same as that of the crystal as a whole. Results given in table 4 (p. 561) illustrate this clearly.

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[1] *Proc. Phys. Soc. London*, **57**, 477, 1945.

[2] Owen and Yates. *Phil. Mag.*, **17**, 113, 1934.

[3] Jay, *Proc. Roy, Soc.*, **143**, 465, 1934.

[4] Jay, *Proc. Roy. Soc.*, **142**, 237, 1933.

There are some workers[1] who hold the opposite view. Recently, however, Austin, Saini Weigle and Pierce[2] have observed that the measurements by the X-ray and optical interferometer methods on the same specimen of calcite gave values which are the same, within limits of experimental error. They further observed that the expansion is different for different samples of calcite.

Table 4.—Coefficient of expansion of some crystals in the range 0°—100°C.

Substance	Microscopic		Macroscopic	
	Parallel to axis	Perpendicular to axis	Parallel to axis	Perpendicular to axis
Zn	$14 \cdot 3 \times 10^{-6}$	$60 \cdot 8 \times 10^{-6}$	$14 \cdot 1 \times 10^{-6}$	$63 \cdot 9 \times 10^{-6}$
Bi	16·9	11·9	16·3	
Ag	19·1		19·1	11·8
Pt	8·68		8·94	

EXPANSION OF LIQUIDS

13·18. In case of liquids we have to consider only the cubical expansion. As before, the volume can again be expressed as a function of the temperature; thus

$$V = V_0 (1 + \alpha_1 t + \alpha_2 t^2 + \ldots\ldots), \quad . \quad . \quad . \quad (16)$$

or approximately,

$$V = V_0 (1 + \alpha t). \quad . \quad . \quad . \quad . \quad (17)$$

The expansion of liquids is much greater than that of solids, yet it is more difficult to measure, for it is complicated by the expansion of the containing vessel. The expansion observed is called the apparent expansion and is a resultant of the two effects, *viz.*, expansion of the liquid and of the containing vessel. It can be shown that the coefficient of absolute expansion of the liquid is approximately equal to the sum of the coefficients of expansion of the containing vessel and the coefficient of apparent expansion of the liquid. Thus the former can be determined if the latter two quantities are known.

There are three well-known methods for determining the *apparent* or *relative expansion* :—

(i) The Volume Thermometer method, (ii) the Weight Thermometer method and (iii) the Hydrostatic method.

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[1] Goetz and Hergenrother, *Phys. Rev.*, **40**, 643, 1932.

[2] *Phys. Rev.*, **57**, 934, 1940.

13·19. The Dilatometer or Volume Thermometer Method.—The volume thermometer consists of a bulb to which a graduated stem is attached. It is nearly filled with the experimental liquid whose levels on the stem are observed at temperatures 0° and t°C. If the liquid stands up to the mark x_0 on the stem at 0°C and up to the mark x_1 at t°C, and if the volume of the bulb at 0°C is V_0 and of each division of the stem v_0, then the volumes of the liquid at the two temperatures are

$$V_0+x_0v_0 \text{ and } (V_0+x_1v_0)\,(1+\gamma t),$$

γ being the expansion of the containing vessel. The volume at t°C is also equal to

$$(V_0+x_0v_0)\,(1+\alpha t),$$

where α is the coefficient of absolute expansion of the liquid. Equating we have

$$(V_0+x_0v_0)\,(1+\alpha t)=(V_0+x_1v_0)\,(1+\gamma t). \quad . \quad . \quad (18)$$

Knowing γ the true coefficient α can be calculated, or if γ is not known, the relative expansion $\alpha-\gamma$ can be evaluated.

13·20. The Weight Thermometer Method.—A more accurate method, depending upon the determination of weights and not of volumes, is furnished by the weight thermometer. The thermometer is of the shape shown in Fig. 13 and is made of glass or fused silica. It is first weighed and then completely filled with the liquid by alternate heating and cooling with the open end dipping in a cup of the liquid. Some air often adheres to the neck of the thermometer; to remove it completely the liquid in the thermometer is boiled until half of it is evaporated and then cooled. The process may be repeated. The experiment consists in weighing the thermometer filled with the liquid at two temperatures.

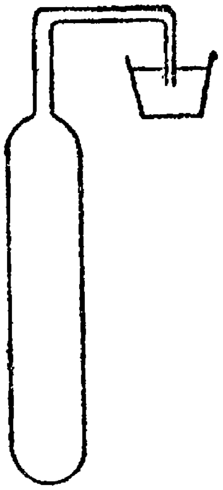

Fig. 13.—The Weight Thermometer

Let w_1, w_2 represent the weights of the liquid filling the thermometer at temperatures t_1 and t_2 respectively. If V_1, V_2 are the volumes of the vessel at the two temperatures and ρ_1, ρ_2 the corresponding densities of the liquid, then

$$w_1=V_1\rho_1, \quad w_2=V_2\rho_2. \quad . \quad . \quad . \quad . \quad (19)$$

But if α and γ denote expansion coefficient of the liquid and the vessel respectively, then

$$\frac{V_2}{V_1}=\frac{1+\gamma t_2}{1+\gamma t_1}; \quad \frac{\rho_2}{\rho_1}=\frac{1+\alpha t_1}{1+\alpha t_2}.$$

Hence from (19),

$$\frac{w_1}{w_2} = \frac{1+\gamma t_1}{1+\gamma t_2}\,\frac{1+\alpha t_2}{1+\alpha t_1} = \frac{1+\alpha\,(t_2-t_1)}{1+\gamma\,(t_2-t_1)} \text{ approx.}$$

Multiplying out we obtain

$$w_1\,[1+\gamma(t_2-t_1)] = w_2\,[1+\alpha(t_2-t_1)]. \qquad (20)$$

whence

$$\alpha-\gamma = \frac{w_1-w_2}{w_2\,(t_2-t_1)}\,. \qquad (21)$$

Knowing γ, the absolute expansion α can be calculated.

The thermometer can also be employed to find the cubical expansion of solids indirectly by enclosing the specimen inside the thermometer.[1]

13·21. Hydrostatic Method.—This consists in finding the apparent weight of a solid when immersed in the liquid at two temperatures t_1, t_2 respectively. The loss in weight of the solid is by Archimedes' principle equal to the weight of a volume of the liquid equal to that of the solid; denote this quantity by w. Then

$$w_1 = V_1\,\rho_1, \quad w_2 = V_2\,\rho_2,$$

where V_1, V_2 denote the volumes of the solid at the two temperatures t_1, t_2 respectively. Then

$$\frac{V_1}{V_2} = \frac{1+\gamma t_1}{1+\gamma t_2}, \quad \frac{\rho_1}{\rho_2} = \frac{1+\alpha t_2}{1+\alpha t_1};$$

and proceeding as before,

$$\alpha-\gamma = \frac{w_1-w_2}{w_2(t_2-t_1)}\,. \qquad (22)$$

13·22. Absolute Expansion of Liquids.—As already mentioned, the three foregoing methods may be employed to find the absolute expansion of a liquid provided the cubical expansion of the containing vessel (or of the immersed solid in §13·21) be known. One way of finding the latter is by calculating it from the linear expansion. This is, however, open to objection for the linear expansion is determined from experiments with bars of the material and it cannot be assumed *à priori* that the physical properties of the material do not change when it is annealed and worked into a vessel of some shape. For this reason it is best to select vessels of fused silica for which the volume coefficient is extremely small (about 0·0000015).

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[1] See Glazebrook, *A Dictionary of Applied Physics*, Vol. 1, p. 878.

13·23. Hydrostatic Balance Method.—There is only one direct method of determining the absolute expansion of a liquid which was first given by Dulong and Petit.[1] It depends on the hydrostatic balancing of two liquid columns at different temperatures. Dulong and Petit employed a simple U-tube for the purpose. Regnault brought the upper ends of the tube close together, an improvement which made it easier to observe the difference in height of the two columns. The diagram (Fig. 14) serves to illustrate the principle of the method. A glass or metal tube, bent as shown in the figure, contains mercury. The vertical columns AB, CD, C′D′ are surrounded by melting ice and are thereby maintained at 0°C., while the column A′B′ is surrounded by an oil bath maintained at any temperature t°C. Suppose that AA′ is horizontal. Let H, H', h, h' denote the heights of mercury in the various columns as shown, and ρ, ρ_0 the densities of mercury at t°C and 0°C. Then, since the pressures at D and D′ are equal, we have by equating the two expressions for the hydrostatic pressure at A

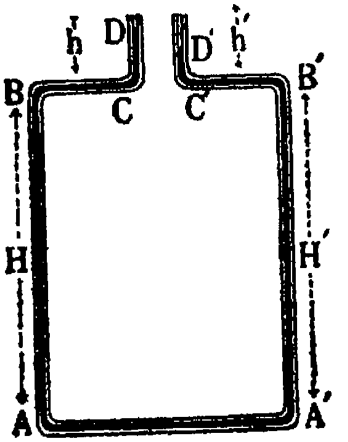

Fig. 14—The Hydrostatic Balance Method.

$$h'\rho_0 + H'\rho = H\rho_0 + h\rho_0 \quad . \quad . \quad . \quad . \quad (23)$$

But $$\rho = \rho_0/(1+ct),$$

where c is the coefficient of absolute expansion of mercury. Hence

$$\frac{H'}{1+ct} + h' = H + h, \quad . \quad . \quad . \quad . \quad (24)$$

from which c can be calculated.

If the columns H, h, h' are not at 0°C, but at temperatures t_1, t_2, t_3 respectively, we shall get

$$\frac{H'}{1+ct} + \frac{h'}{1+c_{t_3}t_3} = \frac{H}{1+c_{t_1}t_1} + \frac{h}{1+c_{t_2}t_2} \quad . \quad . \quad (25)$$

where the quantities c_{t_1}, c_{t_2}, c_{t_3} denote the mean coefficients of expansion between the ranges 0—t_1, 0—t_2 and 0—t_3 respectively. These can be determined by performing three experiments in which the column A′B′ is maintained at temperatures t_1, t_2 and t_3 respectively. If the height of A′ above A is h_1, a corresponding term can be added to the right-hand side.

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[1] *Ann. Chim. Phys.*, (2), 7, 127, 1818.

Regnault's observations, though carried out with great skill must be corrected for various sources of error and hence, cannot yield results of high accuracy. Callendar and Moss[1] repeated the experiments aiming at a high degree of accuracy. Instead of a single pair of hot and cold columns 1·5 m. long employed by Regnault, they used six pairs of hot and cold columns each 2 m. long and connected in series as shown diagrammatically in Fig. 15. The hot and cold columns are marked H and C respectively. The difference in height of the first and the last columns (*viz.*, *ab*) is six times that due to a single pair.

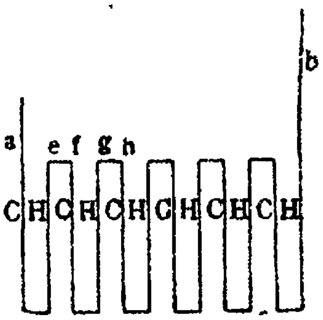

Fig. 15.—Arrangement of Callendar and Moss's apparatus.

In the actual apparatus ef, gh,. . . were doubled back so that all the columns marked C were one behind the other; and similar was the case with the H columns. All the H columns were placed in one limb of a rectangle and all the C columns in one limb of another rectangle, while the other limbs of these rectangles contained electrically heated oil and ice-cooled baths respectively. These were kept circulating by means of an electric motor and their temperatures were determined by a long 'bulb' resistance thermometer. Experiments were performed in the range 0 to 300°C. An accuracy of 1 in 10,000 was aimed at. For this various precautions had to be taken. For full details see *Dictionary of Applied Physics*, Vol. I, p. 880. Chappuis[2] also found the absolute expansion of mercury by the same method.

13·24. Results for Mercury.—The experimental results for mercury have been collected together by Harlow.[3] Among the more accurate determinations are those by Callendar and Moss by the hydrostatic balance method, those by Chappuis and Harlow[4] by the weight thermometer method and that of Chappuis by the hydrostatic balance method.

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[1] *Phil. Trans.*, **7**, 674, 1929.

[2] *Trav. et Mem. du Bur. Int.*, **16**, 1917.

[3] *Phil. Mag.*, **7**, 674, 1929.

[4] *Proc. Phys. Soc. Lond.*, **24**, 30, 1911.

Harlow has also made accurate determinations with the help of a weight thermometer of silica and aimed at an accuracy of 1 in 18,000. The concordance of results with bulbs of different shapes showed that silica was quite isotropic. The results of Chappuis by both methods and of Harlow agree among themselves and hence, appear to be more accurate than those of Callendar and Moss. According to Chappuis the mean coefficient of expansion of mercury between 0° and 100°C is 0·0001820.

13·25. Expansion of Water.—It is well known that the expansion of water is anomalous in the region 0° to 4°C. When water at 0°C is heated it goes on contracting as long as the temperature is below 4°C. Above 4°C it expands on heating. This anomalous behaviour is explained on the assumption that there exist three types of molecules H_2O, $(H_2O)_2$, $(H_2O)_3$, which have different specific volumes and are mixed in different proportions at different temperatures. The total volume occupied is assumed to be the sum of the specific volumes, though there seems to be scanty justification for such an assumption.

13·26. Expansion of Gases.—The expansion of gases at constant pressure and at constant volume has been treated in Chapter I and forms the very basis of the system of thermometry adopted. The subject has again been dealt with in Chapter X and will not be considered further.

13·27. Effect of Pressure on the Coefficient of Expansion.—Since the volume of a substance is affected by a change in pressure it is obvious that the volume coefficient of expansion must depend upon the pressure. The exact dependance can be easily deduced. Assuming that the volume of the substance at a certain temperature and pressure is always the same and is independent of the manner in which the change is brought about, it follows that dv is a perfect differential, i.e.,

$$\frac{\partial}{\partial T}\left(\frac{\partial v}{\partial p}\right)_T = \frac{\partial}{\partial p}\left(\frac{\partial v}{\partial T}\right)_p$$

Or

$$-\left(\frac{\partial \kappa}{\partial T}\right)_p = \left(\frac{\partial \alpha}{\partial p}\right)_T, \quad . \quad . \quad . \quad . \quad (26)$$

where α and κ denote the coefficient of expansion and compressibility of the substance respectively. Thus if the compressibility increases with rise of temperature, the coefficient of expansion will decrease with increase of pressure. In case of mercury from Bridgman's data we have

$$\left(\frac{\partial \kappa}{\partial T}\right)_p = 7\times10^{-9} \text{ atmos. per deg.}$$

$$\left(\frac{\partial a}{\partial p}\right)_T = 7\times10^{-9} \text{ per atmos.}$$

Thus, the effect of pressure on expansion is very small. If α at 1 atmosphere pressure is $1\cdot82\times10^{-4}$, then at 10 atmospheres pressure α will be equal to $1\cdot8207\times10^{-4}$.

PROBLEMS

1. The expansion of a platinum wire 1·5 mm. in diameter is studied with a Fizeau's apparatus. When the furnace containing the wire is heated from 30°C to 280°C, it is found that 12·5 fringes of the mercury green line 5461 Å. U. shift across the cross-hair in the field of view. Calculate the average coefficient of linear expansion of platinum.

2. With Mo Kα X-rays of wave-length 0·7078 Å. U. incident on a certain set of atomic planes in tungsten at 30°C, a Bragg glancing angle of 65°6′ was observed. When the tungsten was heated to 230°C, the glancing angle became 65°0′. Calculate the coefficient of expansion of tungsten.

Books Recommended.

1. Glazebrook, *A Dictionary of Applied Physics*, Vol. 1, pp. 872-900.
2. Müller-Pouillets, *Lehrbuch der Physik*, Vol. 3, Part 1, pp. 301-310.
3. *Handbuch der Physik*, Vol. 10, pp. 52-59.

CHAPTER XIV

CONDUCTION OF HEAT

14·1. Methods of Heat Propagation.—When a bar of metal is heated at one end and held at the other by the hand we feel the sensation of heat. Heat travels from the hot end along the bar and produces this sensation in the hand. The power of transmitting heat in this manner is possessed by all substances to a varying degree and this phenomenon is called *conduction of heat.* In the process of *convection*, heat is transferred by the actual motion of heated particles of matter whether liquid or gaseous. This is best illustrated by placing gently some crystals of potassium permanganate at the bottom of a beaker containing water and heating the beaker at the bottom. Heated water rises up and curls down forming a closed path which is rendered visible by the red colour imparted to the water. In conduction, heat is transferred 'by contact' and there is no apparent transfer of matter.

In both the above processes, the intervening medium takes an active part in heat propagation, but there is a third process in which the intervening medium takes no part. If we stand near a coal furnace, we feel the sensation of heat. If we are in the sun, we feel warm. Here the source of heat is the coal furnace or the sun, and in the latter case it is at an enormous distance from us. There is absolutely no material medium in the space between us and the sun excepting the thin atmospheric layer, still heat from the sun continues to reach us. This phenomenon is called *Radiation.* The processes of conduction and convection are necessarily slow due to the action of the intervening medium but radiation, as we shall see later, travels with the enormous velocity of light. In this chapter we shall consider only the conduction of heat.

14·2. Definition of Conductivity.—A precise definition of conductivity was first given by Fourier in his memorable *Théorie analytique de la chaleur* (1822). We shall first discuss the flow of heat inside a bar heated at one end. Consider a thin wall of the material with parallel faces such that heat flows in a direction perpendicular to the faces. Let θ_1, θ_2 denote respectively the temperatures of the near and the distant face, l the thickness of the wall and A the area of each face. Then it can be shown experimentally that the amount of heat Q flowing out through the wall from the near face to the more distant face in a time t, when the temperature at every point of the bar is steady, is directly proportional to (i) the temperature difference $(\theta_1-\theta_2)$, (ii) the area A of the surface, (iii) the time t and (iv) inversely proportional to l. We have therefore

$$Q = KA\,\frac{\theta_1-\theta_2}{l}\,t. \qquad \text{. . . . . (1)}$$

The coefficient K is a quantity depending upon the nature of the substance and is called its *thermal conductivity.* From this relation conductivity may be defined as *the quantity of heat flowing per second through a unit area of plate of unit thickness, when the difference of temperature between the faces is unity.* In analogy with the electrical resistance, the inverse of K may be called the *thermal resistance* of a unit cube.

Now imagine the thickness of the plate to be diminished indefinitely. The limiting value of $\frac{\theta_1-\theta_2}{l}$ or $-\frac{\theta_2-\theta_1}{l}$ is $-\frac{d\theta}{dx}$. The quantity $d\theta/dx$ denotes the temperature gradient at the point in question directed along the normal to the surface. The minus sign has been used before $d\theta/dx$ because the symbol d always stands for the increase. Hence the quantity of heat dQ flowing in the positive direction of x in time dt across the isothermal surface of area A at any point x is given by

$$dQ = -KA\,\frac{d\theta}{dx}\,dt, \qquad \text{. . . . . (2)}$$

and the thermal current is

$$\frac{dQ}{dt} = -KA\,\frac{d\theta}{dx} = -\frac{d\theta}{\Psi}, \qquad \text{. . . . (3)}$$

where Ψ may be called the thermal resistance. (3) is analogous to Ohm's law in electricity.

Equation (2) is of fundamental importance in the theory of heat conduction. The units in which conductivity is measured on the C.G.S. system are the calorie per second per square centimetre of area for a temperature gradient of 1°C per cm. (cal. cm.$^{-1}$ sec.$^{-1}$°C^{-1}.) It may also be expressed in watts per cm. per degree.

CONDUCTIVITY OF METALS

We shall now give the various methods[1] of determining the thermal conductivity of metals. Methods I to IV employ stationary heat-flow while in V a stationary periodic flow of heat and in VI a variable aperiodic flow is employed.

I. Conductivity from Calorimetric Measurement

14·3. Conduction in Rods with negligible or no lateral leakage.—The definition of conductivity from equation (1) provides a simple method of determining the conductivity of a substance. We need have only a slab of the material of known cross-section heated at one end and measure the amount of heat that flows out at the other end in a known time, as well as the temperature of the two faces. Thus all the other quantities except K in equation (1) is known, and hence K can be evaluated.

The method though simple presents some experimental difficulties. It is found difficult to measure accurately the temperature of the two faces of a slab of metal. This is best achieved by keeping embedded in the surface the junction of a thermocouple, the use of mercury thermometer or resistance thermometer being inconvenient or impossible. Some early experimenters used steam to heat the slab at one end and ice or water to cool it at the other end, and assumed that the temperature of the end faces of the slab was that of steam and water respectively. But if proper precautions be not taken, this procedure is liable to give absurd results because a thin film of fluid, always at rest, is formed in contact with the surface, and this has a large temperature gradient. Hence it is essential that we should observe the temperature inside the slab itself by means of thermometers. There are many apparatus based on this method and one due to Searle is described below.

Fig. 1 shows the apparatus diagrammatically. One end B of the rod AB is enclosed in the steam-chamber S while the other end A projects into another chamber C through which cold water circulates as indicated, the temperatures at entry and exit being T_3 and T_4 respectively. Temperatures at two points along the bar are measured by thermometers T_1

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[1] For a brief survey of the various methods in practical use see Ezer Griffiths, *Proc. Phys. Soc. Lond.*, **41**, 151, 1928.

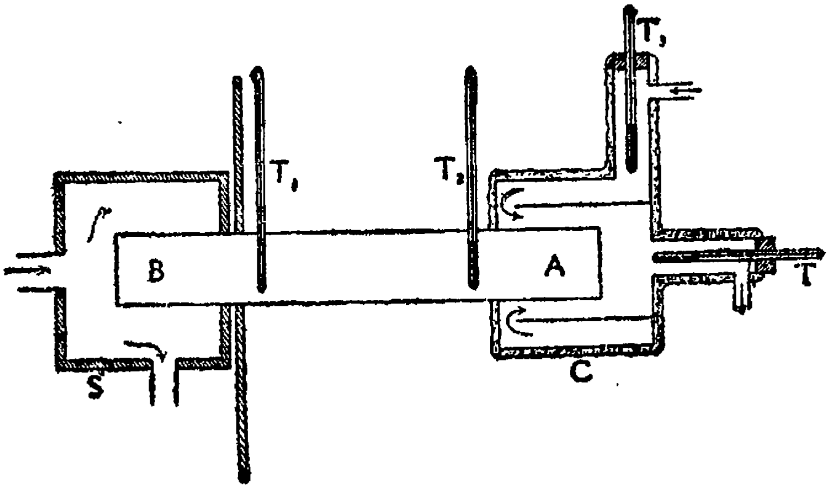

Fig. 1.—Searle's Apparatus.

and T_2; let these be T_1 and T_2. The whole rod is wrapped round with some non-conducting material like wool, felt, cork shaving, etc. In the steady state if m grams of water flow past the cold end of the bar per second, the heat conducted by the bar per second is $m(T_4-T_3)$, and this equals $KA\ (T_1-T_2)/d$, where d is the distance between the thermometers T_1, T_2. Thus the conductivity K is determined.

14·4. The Guard-ring Method.—In the foregoing experiment some heat was lost by radiation from the sides of the bar. This is a source of error and is very easily eliminated if the bar be surrounded with some material at the same temperature as the adjacent portions of the bar. There will be no flow of heat perpendicular to the length of the bar as no temperature gradient exists in that direction. This surrounding material prevents the flow of heat and is usually referred to as the 'guard-ring'.

Berget[1] utilised this guard-ring method for determining the conductivity of various substances such as copper, iron, brass and mercury. A vertical cylindrical column of mercury is surrounded by an annular ring of mercury. In both the upper surface of mercury is heated by steam while the lower surface rests on a metal plate cooled by ice. Thus the temperature gradient as well as the temperatures at the same level in the experimental column and the surrounding annular ring are identical. Under these conditions there can be no lateral flow of heat and the annular ring serves as a 'guard-ring'. The lower end of the experimental column projects into the bulb of a Bunsen ice-calorimeter and the heat flowing out at this end is found from the indications of the mercury thread. The difference of temperature between several points along the column is determined by four differential thermocouples. The conductivity K can be calculated from the formula

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[1] *Journ. de Phys.*, 7, 503, 1888.

$$K = \frac{Q}{At} \cdot \frac{x}{\theta_1 - \theta_2} . \qquad (4)$$

The guard-ring method is very simple and convenient and at the same time accurate, and has consequently been employed by various workers. A suitable form of apparatus was employed by Donaldson[1] in which the heating is done electrically. His apparatus is shown in Fig. 2.

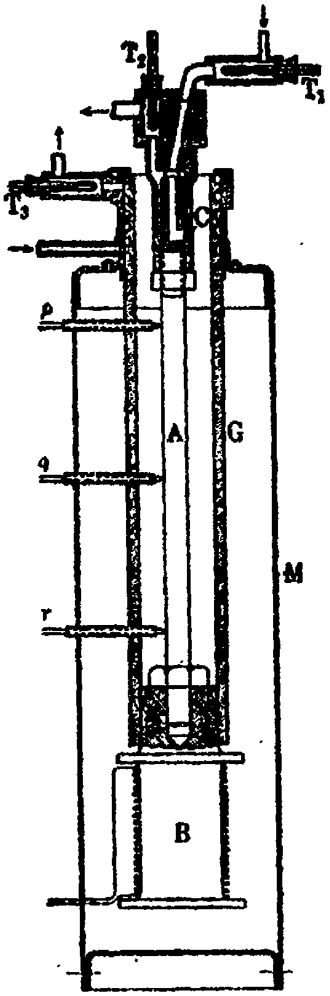

Fig. 2.—Donaldson's Apparatus.

The experimental rod A has its lower end placed in contact with the electrically heated body B while the upper end projects into a continuous-flow water calorimeter C. The amount of heat flowing axially along the rod was obtained from a knowledge of the difference of temperature between the inflowing and outflowing water as indicated by the thermometers T_1, T_2. The experimental rod was completely surrounded by a cylindrical concentric guard-ring G made of the same material but separated from it by an air-space. The guard-ring also had its lower end placed in contact with the same heater B while its upper end facing the calorimeter was cooled by another current of water at the same temperature as the inflow water of the calorimeter. By regulating the flow of water and with the help of the thermometer T_3 it was so arranged that the temperature gradient in the guard-ring was exactly the same as in the experimental rod. Thus the temperatures at the same level in the rod A and the guard-ring are identical and there will be absolutely no loss of heat from A sideways. The temperature gradient along the bar is obtained from the readings of the thermocouples *p*, *q*, *r* which have their junctions fixed in the rod. The whole apparatus is thermally insulated by the cover M. The calculation is similar to that in Searle's experiment.

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[1] See Jakob, *Zeits. f. Metallkde.*, **18**, 55, 1926,

14·5. Again the amount of heat passing through the experimental rod can be known electrically. Electrical energy is supplied to a separate heating body from which it is allowed to flow along the rod. The energy supplied can be calculated from the values of the current and the voltage. This method was given by Lees[1] and others for finding the conductivity of badly conducting solids and liquids. Using this method Lees[2] found the conductivity of metals down to liquid air temperatures. Jakob[3] designed an apparatus which was originally meant for determining the conductivity of liquids, but is also suitable for measuring the conductivity of metals provided the heater is properly designed. Such an apparatus is shown in Fig. 3.

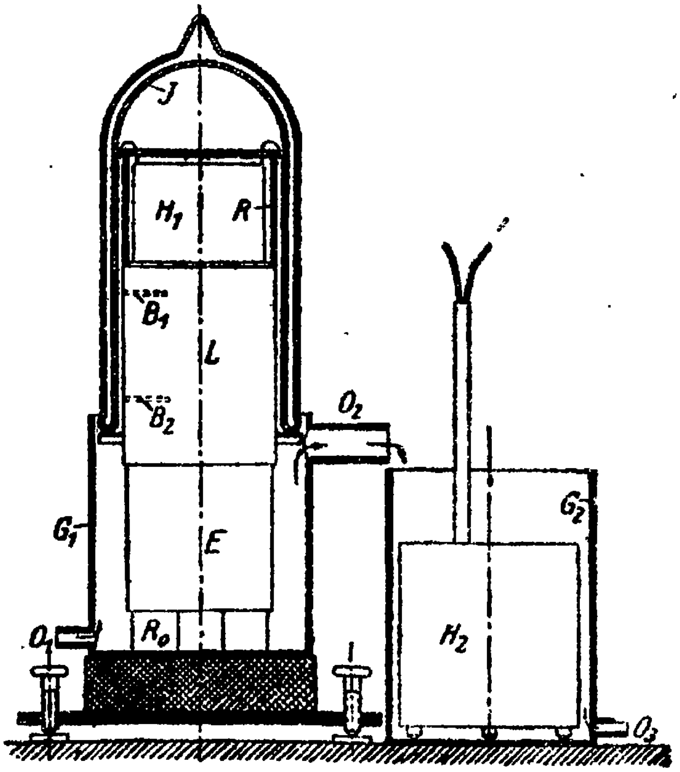

Fig. 3.—Jakob's apparatus for finding conductivity.

Heat is generated in the electrical heater H_1, and passes axially downwards through the vertical experimental cylinder L and then through the iron block E to the cooling water. This water can be maintained at any temperature between 0° and 100°C by cooling with ice or heating by means of the electrical heater H_2. The same water is maintained in circulation through $O_1G_1O_2G_2O_3$ and back again to O_1, by means of a small pump. R is a metal cap which serves as the first mantle against loss of heat by radiation from the heater. The temperature of H_1 can be maintained constant. The vacuum mantle J is a second protection against heat loss. At B_1 and B_2 temperatures T_1, T_2 are measured by two thermo-elements. The amount of energy Q added can be obtained from the electrical energy given to the heater minus the heat lost. The heat loss can be obtained from auxiliary experiments.

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[1] *Phil. Trans.*, **19**, 399, 1898. [2] *Phil. Trans.*, **208**, 381, 1908.

[3] *Zeits. d. Ver. d. Ing.*, **66**, 688, 1922; *Wiss. Abh. d. Phys. Techn. Reichsanst.*, **6**, 137, 1923.

Certain modifications of the method have been made by some Japanese workers. Honda and Simidu[1] have employed the well-known "two-plate" method for determining the thermal conductivity of metals. The arrangement of the "two-plate" system employed by them is shown in Fig. 4. P_1 and P_2 are two exactly similar plates made of the experimental material. Between these is symmetrically placed the electrical heater H in which the heat Q is generated. For perfect symmetry two cold plates K, K, maintained at the same temperature, are placed at the other ends of these plates. Thus the amount of heat flowing through each plate is $Q/2$.

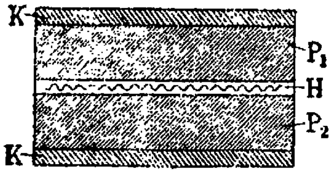

Fig. 4.—The two-plate system.

14·6. Measurement of Conductivity at Very Low Temperatures.—As already mentioned, Lees used the rod method for measuring the conductivity of many metals throughout the temperature range 18°C to —170°C. The experimental rod was heated electrically at one end, its other end being fixed to the base of a hollow, closed, cylindrical shell of copper which completely surrounded the rod. The outer cylinder was immersed in liquid air or heated electrically and thus the desired temperature of experiment was attained. Knowing the electrical energy spent and the temperature at two points on the rod the thermal conductivity can be calculated. Some corrections are however necessary which are difficult to evaluate accurately.

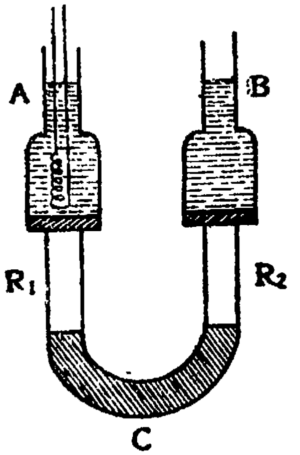

Fig. 5.—De Haas' apparatus for conductivity at liquid helium temperatures.

Since 1930 thermal conductivity measurements have been extended to liquid hydrogen and liquid helium temperatures by W. J. de Haas[2] and his coworkers. Fig. 5 shows the essential features of de Haas' apparatus for measuring the thermal conductivity at liquid helium temperatures. The experimental substance is in the form of two rods R_1, R_2 mounted between the copper yoke C and the two reservoirs A and B containing liquid helium. The whole apparatus was enclosed in a chamber kept at the desired low temperature, the chamber itself being highly evacuated. Heat was generated electrically in the heating coil placed in the reservoir A, this heat being transferred almost wholly by conduction through R_1, C, R_2 to B. The reservoirs A and B formed part of two vapour pressure thermometers so that their temperatures could be measured and kept constant by regulating the current in the heating coil in A and by pumping off the vapour in B thereby causing the liquid in B to boil at the proper rate. The conductivity could be easily calculated from a knowledge of the heat generated in the coil and the conductivity of the yoke C.

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[1] *Sci. Reports, Tohoku Univ.*, **6**, 216, 1917.

[2] De Haas and Bremmer, *Leiden Commun.*, No. 214, p. 45, (1931).

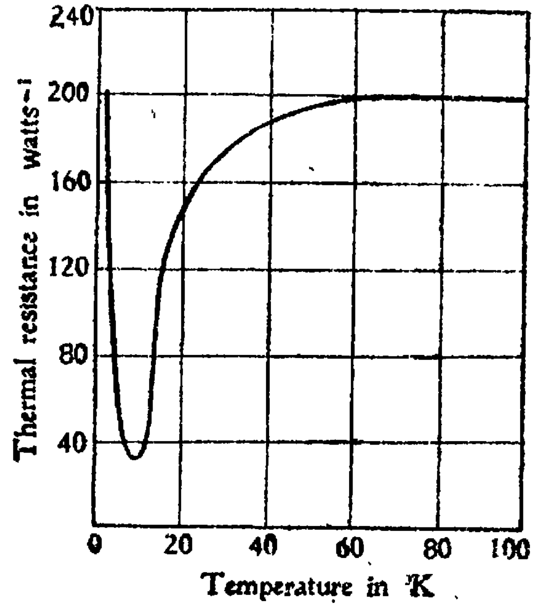

Fig. 6.—Thermal resistance of lead.

The results of de Haas for lead are shown in Fig. 6. The thermal resistance begins to decrease as the temperature is lowered below 50°K reaching a minimum at about 9°K and thereafter again increases rapidly. Similar results are obtained with several other substances.

II. Conductivity from Temperature Measurement—Indirect Method.

14·7. Rectilinear flow of heat. Mathematical Investigation—

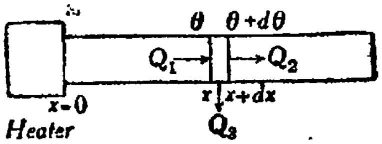

Fig. 7.—Flow of heat in a rod.

Consider a metal rod heated at one end, the isothermal surfaces being parallel planes perpendicular to the length of the rod, and let the axis of x be normal to these planes. Let θ be the temperature at a distance x from the hot end (Fig. 7) and $\frac{d\theta}{dx}$ be the temperature gradient. Consider a layer of thickness dx at this point. The amount of heat Q_1, which enters the layer per second is $-KA\dfrac{d\theta}{dx}$ (from equation 2), Q_2 the heat which leaves the layer at the face $x+dx$ is

$$-KA\,\frac{d}{dx}\left(\theta+\frac{d\theta}{dx}dx\right),$$

since $\theta+\dfrac{d\theta}{dx}dx$ is the temperature of that face. Hence the gain of heat by the layer is equal to

$$-KA\frac{d\theta}{dx}-\left[-KA\frac{d}{dx}\left(\theta+\frac{d\theta}{dx}\,dx\right)\right]=KA\frac{d^2\theta}{dx^2}\,dx.$$

Now before the steady state is reached this amount of heat raises the temperature of the layer of thickness dx. Let ρ be the density and c the specific heat of the material per unit mass, and let the rate of rise of temperature be denoted by $d\theta/dt$. The mass of the layer is $\rho A\,dx$. Hence if we neglect the heat lost by radiation from the surface

$$KA\frac{d^2\theta}{dx^2}\,dx=\rho A dx.\,c\frac{d\theta}{dt}. \quad . \quad . \quad . \quad . \quad (5)$$

$$\therefore\frac{d\theta}{dt}=\frac{K}{\rho c}\cdot\frac{d^2\theta}{dx^2}=h\frac{d^2\theta}{dx^2}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $h=K/\rho c$. h is thus equal to the thermal conductivity divided by the thermal capacity per unit volume, and consequently determines the rapidity with which temperature changes take place in a given rod. This constant has been called *diffusivity* by Kelvin and *thermometric conductivity* by Maxwell; the former term is more commonly used.

If, in addition, the sides of the bar are allowed to lose heat by radiation, this must be taken into account. If E is the emissive power of the surface, p its perimeter and θ the excess of the temperature of the surface over that of the surroundings, this radiation loss Q_3, assuming Newton's Law of cooling to hold true, is equal to $Ep\theta\,dx$. Hence we should rewrite (5) as

$$KA\frac{d^2\theta}{dx^2}dx=\rho A\,dx.\,c\frac{d\theta}{dt}+Ep\theta\,dx,$$

or

$$\frac{d\theta}{dt}=h\frac{d^2\theta}{dx^2}-\mu\theta, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where

$$\mu=\frac{Ep}{\rho Ac}.$$

This is the standard Fourier equation for one-dimensional flow of heat and any problem in thermal conduction along a rod consists simply in the solution of this differential equation for specified boundary conditions.

Steady State.—A state is said to be steady when the temperature at every point of the rod is stationary, *i.e.*, $d\theta/dt=0$. We have then

$$\frac{d^2\theta}{dx^2}=\frac{\mu\theta}{h}=m^2\theta, \quad . \quad . \quad . \quad . \quad (8)$$

where $$m^2=\frac{\mu}{h}=\frac{Ep}{AK}.$$

If the radiation losses from the sides can be neglected, this equation further reduces to

$$\frac{d^2\theta}{dx^2}=0.$$

The solution of this differential equation yields

$$\theta=Ax+B,$$

where the constants A and B can be determined from the boundary conditions. Let these conditions be (1) $\theta=\theta_0$ at $x=0$, θ_0 being the temperature of the source; (2) $\theta=\theta_1$ at $x=l$. Then

$$\theta=\theta_0-\frac{\theta_0-\theta_1}{l}x,$$

where θ is the temperature at any point x.

If radiation losses are not negligible, the solution will be different. Let us assume that in this case $\theta=e^{nx}$ is the solution. Hence by substitution

$$n^2=m^2, \text{ or } n=\pm m.$$

Therefore the complete solution is

$$\theta=Ae^{mx}+Be^{-mx}. \quad . \quad . \quad . \quad . \quad (9)$$

where A, B are constants.

14·8. Ingen-Hausz's Experiment.—A method of comparing the conductivity of different substances based on this deduction was employed by Ingen-Hausz as early as 1789 and is generally shown as a demonstration experiment. Bars of different substances are coated with wax and have their one end immersed in a hot bath of oil. The wax melts to different lengths along different bars. Before the steady state is reached the temperature at any point depends both on the thermal capacity and the thermal conductivity as indicated by equation (7). This is why initially the temperature wave is observed to travel faster along bismuth than along copper, for the low thermal capacity of the former more than compensates for the larger conductivity of the latter. When the steady state is attained however, the wax is found to melt on the copper over a greater length.

Let $l_1, l_2 \ldots$ denote the lengths along which the wax has melted, θ_0 the temperature of the bath measured above that of the surroundings, and θ_1 the temperature of melting wax similarly measured. If the bars are long enough the temperature at their other ends is the same as that of the surroundings, *i.e.*, $\theta=0$. The complete solution of this problem is represented by equation (9). The boundary conditions for all the bars are (*i*) $\theta=0$ at $x=\infty$; (*ii*) $\theta=\theta_0$ at $x=0$; (*iii*) $\theta=\theta_1$ at $x=l$. By substitution in equation (9) condition (*i*) gives $A=0$. Condition (*ii*) then gives $B=\theta_0$. The solution then becomes

$$\theta = \theta_0 e^{-mx}.$$

Condition (*iii*) then yields

$$\theta_1 = \theta_0 e^{-ml}, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

or

$$ml = \log_e \frac{\theta_0}{\theta_1}.$$

Since $\log_e (\theta_0/\theta_1)$ is the same for all the bars we have

$$m_1 l_1 = m_2 l_2 = m_3 l_3 = \quad . \quad . \quad . = \text{constant},$$

which from the definition of m implies that

$$\frac{K_1}{l_1^2} = \frac{K_2}{l_2^2} = \frac{K_3}{l_3^2} = . \quad . \quad . \quad = \text{constant}, \quad . \quad . \quad . \quad (11)$$

provided the different bars have the same cross-section, perimeter and coefficient of emission. In order to secure the same coefficient of emission the bars are electroplated and polished. Thus we have

$$\frac{K_1}{K_2} = \frac{l_1^2}{l_2^2}. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Therefore the conductivities are in the simple ratio of the squares of the lengths along which the wax has melted, and if the conductivity of one of the bars be known the conductivity of the others can be calculated. This is an indirect method.

14·9. Experiments of Despretz, Wiedemann and Franz.—Despretz[1] as early as 1822, compared the conductivity of two substances by finding out three temperatures at equal distances. The bars were heated at one end and were provided with a number of equidistant holes throughout their entire length. These holes contained mercury in which the bulbs of mercury thermometers were immersed for recording the temperature. The theory of the method is as follows :—

Let the temperature of the bar at distances x, $x+a$, $x+2a$ be θ_1, θ_2, θ_3 respectively. The solution of this problem is given by equation (9). We have by the given conditions :

$$\theta_1 = Ae^{mx} + Be^{-mx}$$
$$\theta_2 = Ae^{m(x+a)} + Be^{-m(x+a)}$$
$$\theta_3 = Ae^{m(x+2a)} + Be^{-m(x+2a)}$$

Therefore by division

$$\frac{\theta_1 + \theta_3}{\theta_2} = e^{ma} + e^{-ma} = 2n \text{ (say)},$$

whence $$e^{ma} = n + \sqrt{n^2 - 1},$$

or $$ma = \log_e (n + \sqrt{n^2 - 1}).$$

The negative sign before the radical is impossible since we observe experimentally that $\frac{\theta_1+\theta_3}{2\theta_2} > 1$, hence $n > 1$, but if we put a negative sign before the radical, the term on the right-hand side becomes less than 1 while e^{ma} is necessarily greater than 1.

If the two bars have the same perimeter, cross-section and coefficient of emission, and if a be the same for both of them,

$$\sqrt{\frac{K_1}{K_2}} = \frac{\log (n_2 + \sqrt{n_2^2 - 1})}{\log (n_1 + \sqrt{n_1^2 - 1})}. \qquad (13)$$

Hence if we know the three temperatures θ_1, θ_2, θ_3 for each bar we can find n_1 and n_2 and thence the ratio of the conductivities of the two bars. Wiedemann and Franz[2] following the same principle devised a more accurate apparatus.

III. Conductivity by a Combination of the Steady and Variable Heat Flow.

14·10. Forbes' Method.—One of the earliest methods of determining the absolute conductivity of a substance is that due to

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[1] *Ann. Chim. Phys.*, **19**, 97, 1822; **36**, 422, 1827.

[2] *Ann. de Chimie*, **41**, 107, 1854.

Forbes[1]. Though simple in principle, it is exceedingly tedious in practice. One end of a long bar (Fig. 8) was heated by being fixed into an iron crucible containing molten lead or silver. A number of thermometers, with their bulbs immersed in holes drilled into the bar, were employed to indicate its temperature throughout its entire length. After about six hours the temperatures at all points become steady and are read on the thermometers. The temperature distribution is indicated by the dotted line in Fig. 8, and will follow the law $\theta = \theta_0 e^{-mx}$. This is called the *statical experiment* since it deals with the steady state of heat flow.

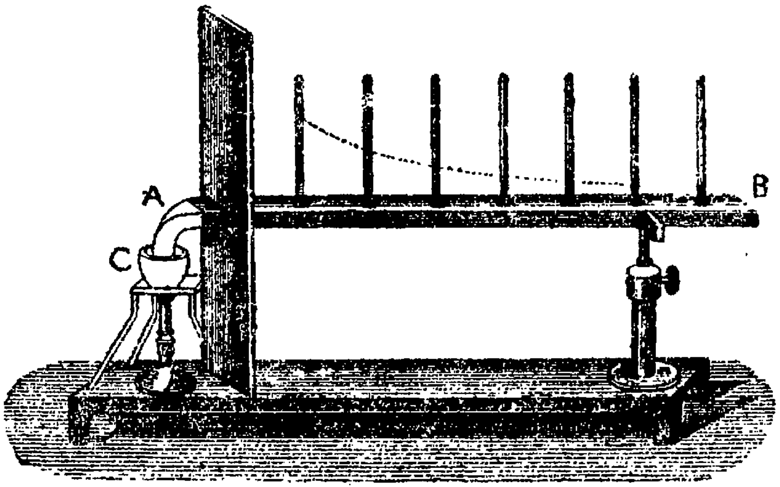

Fig. 8.—Forbes' apparatus. Statical experiment.

To obtain the heat flowing across a particular cross-section Forbes determined the amount of heat lost by radiation by the portion of the bar lying between the cross-section and the cold end. These two quantities are obviously equal in the steady state since no heat flows from the cold end, this being at the room temperature. Forbes achieved it by performing the *dynamical experiment*, so called because the temperature in this case is changing. For this purpose a bar only 20 inches long but in all respects exactly similar to the previous bar was used. First a high uniform temperature is communicated to this bar which is then allowed to cool in exactly the same surroundings as the statical bar, and a cooling curve plotted for it (Fig. 9).

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[1] *Trans. Roy. Soc. Edin.*, **23**, 133, 1864; **24**, 73; 1867.

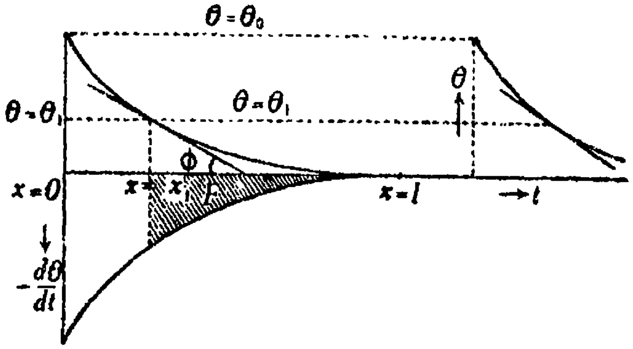

Fig. 9.—Temperature curves in Forbes' bar.

Let us now calculate the amount of heat lost by the statical bar from the point $x=x_1$, to the end of the bar ($x=l$). The amount of heat lost per second by radiation from the surface of the bar from x to $x+dx$ in the steady state, must be equal to

$$-Adx.\ \rho c\frac{d\theta}{dt},$$

where ρ is the density of the material, c its specific heat and $-d\theta/dt$ the rate of cooling of that element. It is so because that very loss of heat produces this cooling of the element by $-d\theta/dt$. Hence the total heat lost by the portion of the bar from $x=x_1$ to $x=l$ in a second is

$$-A\rho c\int_{x=x_1}^{x=l}\frac{d\theta}{dt}\,dx.$$

We suppose that the bar is long enough so that its other end is at the room temperature and hence no heat escapes from the other end. Hence the above expression will be equal to the heat crossing the surface at $x=x_1$ per second, that is,

$$-KA\left(\frac{d\theta}{dx}\right)_{x=x_1}$$

Equating these two quantities we have

$$\frac{K}{\rho c}\left(\frac{d\theta}{dx}\right)_{x=x_1}=\int_{x=x_1}^{x=l}\frac{d\theta}{dt}\,dx. \quad . \quad . \quad . \quad (14)$$

For calculating $d\theta/dt$ the dynamical experiment is performed on an exactly similar specimen with same exposed surface.[1] The observations are plotted as shown in Fig. 9 which is self-explanatory. The θ, x and θ, t curves are drawn from actual observations while the values of $-d\theta/dt$ corresponding to various values of θ are computed from the θ, t curve and plotted as indicated. Equation (14) yields

$$\frac{K}{\rho c}\tan\phi=F, \quad . \quad . \quad . \quad . \quad (15)$$

where ϕ and F are indicated in the figure. The area F of the shaded portion can be measured by means of a planimeter and hence K calculated from (15).

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[1] The slight increase in exposed surface due to the presence of two extra end surfaces produces a negligible effect.

There are several sources of error in Forbes' method. The specific heat does not remain constant for different temperatures as assumed by Forbes. Further the distribution of temperature inside the bar in the statical and dynamical experiments are different. Forbes' method has been improved by Callendar, Nicholson and Griffiths and others. The method is however of little practical value and is mainly of historical and academic interest.

IV. CONDUCTIVITY FROM THE ELECTRICAL ENERGY SPENT ON THE BODY.

14·11. A very good method of directly determining the ratio of the thermal to the electrical conductivity was given by Kohlrausch[1] and the method was experimentally worked out by Jaeger and Diesselhorst.[2] From a knowledge of this ratio and of the electrical conductivity, the thermal conductivity can be found. The theory of the method is as follows :—

When an electric current flows through a straight metallic bar it is heated, and according to Joule's law, the amount of heat generated per second is i^2R watts. This heat will flow sideways, as well as longitudinally, but we suppose that loss of heat from the sides is prevented by the guard-ring or some other device and the two ends of the rod are maintained at definite temperatures. Then the flow may be supposed to be parallel to the axis of the rod. The temperature will be a maximum at some intermediate point O and will fall off to the temperature of the bath at the two ends. Let us find out two points A and B on opposite sides of O where the temperatures are the same, and let the potential fall between A and B amount to ΔE (Fig. 10). Let the difference of temperature between O and A be ΔT. Then it can shown that

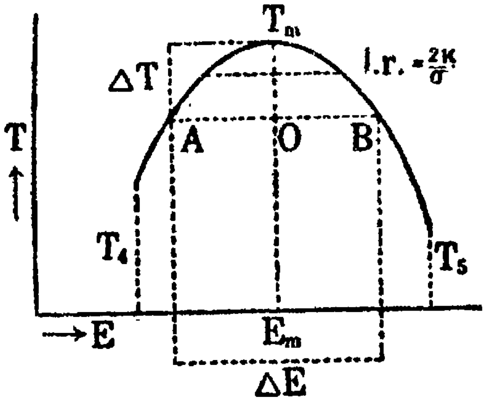

Fig. 10.—Temperature distribution in a rod carrying an electric current.

$$\frac{K}{\sigma} = \frac{1}{8}\frac{(\Delta E)^2}{\Delta T} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

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[1] *Zeits. f. Instrkde.*, **18**, 139, 1898; *Ann. d. Physik*, **1**, 132, 1900.

[2] *Wiss. Abb. d. Phys. Tech. Reichsanstalt*, **3**, pp. 273-290.

If $\triangle E$, $\triangle T$ and σ (electrical conductivity) are measured, K can be calculated by means of this relation.

Equation (16) can be easily deduced. Let us take an element of thickness dx; then the gain in heat in this element due to heat conduction is[1]

$$AK\frac{d^2T}{dx^2}dx.$$

The gain in heat due to the electrical energy supplied is

$$i^2R = A\sigma\left(\frac{dE}{dx}\right)^2 dx, \quad . \quad . \quad . \quad . \quad (17)$$

for

$$R = \frac{dx}{A\sigma}, \quad i = -\frac{dE}{dx}\cdot A\sigma. \quad . \quad . \quad . \quad (18)$$

In case there is no loss of heat from the sides due to radiation, we must have in the steady state, the sum of these quantities of heat equal to zero, *viz.*

$$K\frac{d^2T}{dx^2} + \sigma\left(\frac{dE}{dx}\right)^2 = 0. \quad . \quad . \quad . \quad . \quad (19)$$

Now

$$\frac{dT}{dx} = \frac{dT}{dE}\cdot\frac{dE}{dx}.$$

$$\frac{d^2T}{dx^2} = \frac{d^2T}{dE^2}\left(\frac{dE}{dx}\right)^2 + \frac{dT}{dE}\left(\frac{d^2E}{dx^2}\right).$$

Now since the current i is constant throughout the specimen, and A is also constant it follows that $\sigma\frac{dE}{dx}$ is constant at all points on the bar. Further, if we neglect the variation of σ with temperature and hence with x also, we have $\frac{dE}{dx}$ = constant, or $\frac{d^2E}{dx^2} = 0$. Hence equation (19) after substitution yields

$$\frac{d^2T}{dE^2} + \frac{\sigma}{K} = 0. \quad . \quad . \quad . \quad . \quad (20)$$

Solving the differential equation we get[2]

$$\frac{K}{\sigma}T = -\tfrac{1}{2}E^2 + AE + B, \quad . \quad . \quad . \quad . \quad (21)$$

where A and B are constants of integration.

---

[1] If we take into account the variation of K with temperature and hence with x in this case, this expression will be modified into

$$AK\frac{d^2T}{dx^2}dx + A\frac{dK}{dx}\cdot\frac{dT}{dx}dx.$$

[2] If we take into account the variation of both K and σ with temperature we would get instead of (21) the equation

$$\int\frac{K}{\sigma}dT = -\tfrac{1}{2}E^2 + AE + B.$$

This enables us to find the value of K/σ provided we measure the potential and the temperature at any three points along the bar. Let E_1, E_2, E_3 denote the potentials and T_1, T_2, T_3, the corresponding temperatures. Then by substituting these three sets of values in (21) we get three equations from which on eliminating A and B we get

$$\frac{K}{\sigma}=\frac{1}{2}\cdot\frac{(E_1-E_2)(E_2-E_3)(E_3-E_1)}{T_1(E_2-E_3)+T_2(E_3-E_1)+T_3(E_1-E_2)}. \quad (22)$$

Equation (21) shows that the curve connecting T and E is parabolic (Fig. 9), *viz.*, that the temperature is maximum at a certain point and falls off symmetrically on both sides to the temperature of the bath. There is, however, a constant potential gradient along the bar. If we further choose the intermediate point midway between the extreme points so that $E_2=(E_1+E_3)/2$ and putting $E_1-E_3=\Delta E$ and

$$\frac{(T_2-T_1)+(T_2-T_3)}{2}=\Delta T,$$

equation (22) reduces to

$$\frac{K}{\sigma}=\frac{1}{8}\cdot\frac{(\Delta E)^2}{\Delta T}.$$

If the intermediate point coincides with the point having the maximum temperature, this relation is identical with (16).

In the original apparatus of Jaeger and Diesselhorst, the experimental rod was surrounded by a constant-temperature jacket, hence the expression (16) was corrected for the radial-flow of heat from the wire.

Simidu[1] modified the apparatus in such a way that this correction was rendered unnecessary. His apparatus is diagrammatically shown in Fig. 11. S is the experimental rod at both ends of which the copper wires a_1, a_2 are soldered. B_1, B_2 are two water-baths. M is a guard-ring consisting of a brass tube having a heating spiral H in its middle, and two baths B_3, B_4 at its two ends. V is a vacuum mantle. The whole apparatus is kept inside a wooden chest.

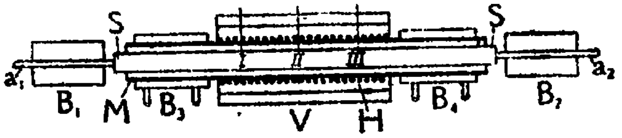

Fig. 11.—Simidu's apparatus for finding K/σ.

Simidu regulates the temperature of B_3, B_4 and the heating current in the coil wound over the brass guard-tube in such a way that at the three points I, II, III, where the temperatures are measured there is no radial flow of heat. He measures the temperatures at I, II, III on the rod, as well as on the inside of the guard-ring by thermo-elements. For a carbon rod the heating current amounted to 10-20 amperes, and the temperature difference varied from 10° to 30°. Masumoto[1] carried out the same experiments with thin rods of aluminium, magnesium, etc. The method has been extended by Meissner[2] to very low temperatures (20°K).

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[1] *Sci. Reports, Tohôku Univ.*, **6**, 111, 1917.

A modification of Kohlrausch's method has been employed by Mendenhall, Angell[3] and Langmuir[4] for measuring conductivity at high temperatures. Angell passed the electric current through a hollow cylinder. Now through a short portion near the centre of the cylinder the axial temperature gradient is very small and the heat flow is only radial. An expression for the conductivity may be obtained by equating the electrical energy supplied to the radial loss of heat by conduction.

V. CONDUCTIVITY FROM PERIODIC FLOW OF HEAT.

14·12. General Discussion.—Uptill now we have considered a steady flow of heat with or without guard-ring. Now we shall discuss the case when one end is periodically heated and cooled. Let us first assume that the temperature at the hot end varies in a simple harmonic manner and the bar is surrounded by a non-conducting material or guard-ring.

The Fourier equation (7) reduces to

$$\frac{d\theta}{dt} = h\frac{d^2\theta}{dx^2}. \qquad \qquad (23)$$

We shall solve the problem by putting

$$\theta = u + v,$$

where u and v satisfy the relations

$$\frac{d^2u}{dx^2} = 0, \qquad \qquad (24)$$

and

$$h\frac{d^2v}{dx^2} = \frac{dv}{dt}. \qquad \qquad (25)$$

From these equations it will be seen that u is a function of x and is independent of t, while v is a function of both x and t.

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[1] *Sci. Reports Tôhoku Univ.*, **13**, 229, 1925.

[2] *Ann. d. Physik*, **47**, 1001, 1915.

[3] *Phys. Rev.*, **33**, 421, 1911.

[4] *Phys. Rev.*, **7**, 151, 1916.

Let us solve (25). If the variation of temperature is given by a simple harmonic function of time, we can assume as solution[1]

$$v = v_0 e^{-\alpha x} e^{i(\omega t + \beta x)} \quad . \quad . \quad . \quad . \quad . \quad (26)$$

It can be readily seen that this represents a damped progressive wave. A progressive wave having the wave-length λ and period T is given by

$$v = v_0 \sin 2\pi\left(\frac{t}{T} - \frac{x}{\lambda} + \epsilon\right).$$

If the wave is damped and the amplitude diminishes according to the exponential law along the x-axis,

$$v = v_0 e^{-\alpha x} \sin 2\pi\left(\frac{t}{T} - \frac{x}{\lambda} + \epsilon\right). \quad . \quad . \quad . \quad (27)$$

Expressions (26) and (27) are equivalent but (26) is preferred in solving the equation for the sake of mathematical convenience. Comparing these two equations we get

$$\frac{2\pi}{T} = \omega, \ \frac{2\pi}{\lambda} = -\beta;$$

and velocity of the wave

$$V = \frac{\lambda}{T} = -\frac{\omega}{\beta}.$$

Thus ω is determined by the periodic time of heating. To find α and β occurring in equation (26) we must substitute the value of v given by (26) in equation (25). We have

$$\frac{dv}{dt} = i\omega v, \ \frac{dv}{dx} = (-\alpha + i\beta)v, \ \frac{d^2v}{dx^2} = (-\alpha + i\beta)^2 v.$$

Hence $\quad i\omega = h(\alpha - i\beta)^2 = h(\alpha^2 - \beta^2 - 2i\alpha\beta).$

$$\therefore \alpha^2 = \beta^2, \text{ and } \omega = -2h\alpha\beta. \quad . \quad . \quad . \quad . \quad (28)$$

Or $\quad \alpha = \pm\beta.$

Now the product $\alpha\beta = -\omega/2h$ is negative, hence α and β must have opposite sign. Thus $\alpha = -\beta$.

Since $\beta = -2\pi/\lambda$, $\alpha = 2\pi/\lambda$. Further

$$h = -\frac{\omega}{2\alpha\beta} = \frac{2\pi}{T} \cdot \frac{1}{2}\left(\frac{\lambda}{2\pi}\right)^2 = \frac{\lambda^2}{4\pi T}, \quad . \quad . \quad . \quad (29)$$

and $\quad V = \frac{\lambda}{T} = 2\sqrt{\frac{\pi h}{T}}; \ \alpha = \frac{2\pi}{\lambda} = \sqrt{\frac{\pi}{hT}}.$

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[1] For discussion of the solution see Ingersoll and Zobel, *Mathematical Theory of Heat Conduction*, p. 38.

The fluctuation of temperature at any point is given by

$$v = v_0 e^{-x\sqrt{\pi/hT}} \sin\frac{2\pi}{T}\left(t - \frac{x}{2\sqrt{\pi h/T}} + \epsilon\right) . \quad . \quad (27a)$$

At any instant the form of this temperature wave is as represented in Fig. 12. At a particular point along the bar (*viz.*, $x =$ constant), θ varies harmonically with time, the period being that of the source. The equation also shows that the amplitude of temperature oscillations at any point diminishes exponentially as the distance x of that point along the bar increases.

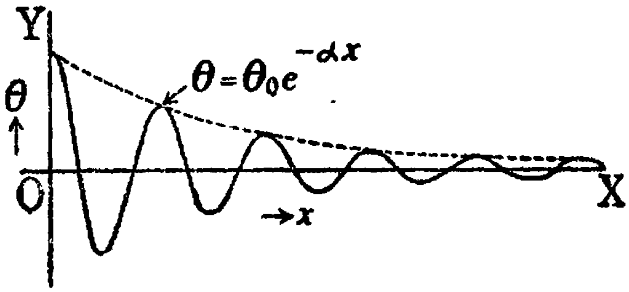

Fig. 12.—Temperature wave at a particular instant.

The solution of (24) gives the steady temperature at any point, and hence also the mean temperature. We have

$$u = \theta_1 - \frac{\theta_1 - \theta_2}{l} x,$$

where θ_1, θ_2 denote the mean temperatures at the ends of the bar. The complete solution is

$$\theta = \theta_1 - \frac{\theta_1 - \theta_2}{l} x + \theta_0 e^{-2\pi x/\lambda} \sin 2\pi\left(\frac{t}{T} - \frac{x}{\lambda}\right) \quad . \quad (30)$$

From equation (29) we can evaluate h and hence the conductivity of the bar, if we measure λ experimentally and determine T.

14·13. Ångström's Experiments.—Angström was the first to determine the conductivity of a bar by periodically heating and cooling it. In his later experiments the end of the bar was enclosed in a chamber through which steam and water at any temperature could be alternately passed. The bar was heated for 12 minutes and cooled also for the same time, the periodic time being 24 minutes. Temperatures were observed every minute at two points along the bar by means of two thermocouples.

In this case, since there is no guard-ring, the Fourier equation is

$$\frac{d\theta}{dt} = h\frac{d^2\theta}{dx^2} - \mu\theta . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The heat applied is only periodic and not simple harmonic, hence the foregoing treatment will not do. However it can be shown that the function representing temperature at any point in a bar can be expanded into a Fourier series of sine and cosine terms. Hence the general periodic solution[1] of (7) is

$$\theta = \sum_{n=0}^{n=\infty} A_n e^{-\alpha_n x} \sin(n\omega t + \beta_n x + \gamma_n). \quad . \quad . \quad . \quad (31)$$

Substituting this value of θ in (7) we get

$$\left.\begin{aligned} \alpha_n\beta_n &= -\frac{n\omega}{2h} \\ \alpha_n^2 - \beta_n^2 &= \frac{\mu}{h} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (32)$$

from which α_n, β_n may be determined and hence the complete solution obtained.

To find the constants A_n, γ_n, the temperatures at two points x and $x+l$ are determined as a function of time as already mentioned. From (31) these can be expressed as

$$\theta_x = \sum_{n=0}^{n=\infty} B_n \sin(n\omega t + \delta_n)$$

and
$$\theta_{x+l} = \sum_{n=0}^{n=\infty} B_n' \sin(n\omega t + \delta_n'),$$

where B_n, B_n', δ_n, δ_n' are constants for the two places and are given by

$$B_n = A_n e^{-\alpha_n x}, \qquad B_n' = A_n e^{-\alpha_n (x+l)}.$$

$$\delta_n = \beta_n x + \gamma_n, \qquad \delta_n' = \beta_n(x+l) + \gamma_n .$$

Hence
$$\alpha_n l = \log_e (B_n/B_n'), \qquad \beta_n l = \delta_n' - \delta_n ;$$

and
$$\alpha_n\beta_n = \frac{(\delta_n' - \delta_n)\log_e (B_n/B_n')}{l^2}.$$

But from (32)
$$\alpha_n\beta_n = -\frac{n\omega}{2h} = -\frac{\pi n}{hT}.$$

$$\therefore h = \frac{n\pi l^2}{T(\delta_n - \delta_n')\log_e (B_n/B_n')} \quad . \quad . \quad . \quad (33)$$

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[1] See Carslaw, *The Conduction of Heat*, p. 42.

Thus the diffusivity and hence the thermal conductivity can be calculated if we know δ_n, δ_n' and B_n, B_n'. Hence we get as many independent values of h as there are terms in (31). Usually the first two or three terms are important as the coefficients diminish rapidly.

The evaluation of the constants $B_n, B_n', \delta_n, \delta_n'$ is quite easy though somewhat tedious. From the above we have

$$\theta_x = \theta_0 + B_1 \sin(\omega t + \delta_1) + B_2 \sin(2\omega t + \delta_2) + \dots$$

$$\therefore \int_{t_1}^{t_1+T} \theta_x \sin \omega t \, dt = \tfrac{1}{2} T B_1 \cos \delta_1 = S_s \text{ (say);}$$

$$\int_{t_1}^{t_1+T} \theta_x \cos \omega t \, dt = \tfrac{1}{2} T B_1 \sin \delta_1 = S_c \text{ (say).}$$

These results can be easily verified if we perform the integration term by term. Hence

$$B_1^2 = \frac{4}{T^2}(S_s^2 + S_c^2); \quad \tan \delta_1 = \frac{S_c}{S_s}.$$

To find the values S_c, S_s of the integrals, first the curve between θ_x and t is plotted from which a second curve between $\theta_x \sin \omega t$ and t, and a third one between $\theta_x \cos \omega t$ and t are drawn. In these curves the area lying between the curve and the t-axis for values lying between $t = t_1$ and $t = t_1 + T$ is measured with a planimeter giving S_c and S_s.

To find any other constant B_n, δ_n we have to multiply by $\sin n\omega t$, and $\cos n\omega t$ and proceed as before. The same process has to be applied to θ_{x+l}.

A modification of Ångström's method was employed by King.[1] One end of the rod is electrically heated, the heating current being varied in a simple harmonic manner by means of a cam. The conductivity is determined from observation of the velocities of two waves of different periods. For details and the theory of the method, the original paper may be consulted.

These investigations have got an important application in determining the extent to which variations in temperature at the earth's surface penetrate into the interior of the earth (see § 14·33).

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[1] *Phys. Rev.*, II, **6**, 437, 1915.

VI. Conductivity by Aperiodic Variable Heating (Non-stationary Flow).

14·14. This method is originally due to Neumann.[1] He heated one end of a rod and then allowed it to cool. The conductivity can be determined by measuring the variation with time of temperatures at the points $x=0$ and $x=l$. The formulae are somewhat complicated.

Kirchhoff and Hansemann[2] extended the case to a cube. But the theoretical calculations as well as experimental procedure have been much simplified by Schulze[3], Grüneisen[4] and Giebe[5]. These investigators introduced one end ($x=0$) of the bar in a hot water bath at temperature θ_0 and observed the rise in temperature at two points on the bar. If we neglect the loss of heat from the sides, we have the equation

$$\frac{d\theta}{dt}=h\,\frac{d^2\theta}{dx^2}. \qquad (34)$$

Let us introduce[6] the variable $\xi=x/2\sqrt{ht}$. Then it can be easily shown that (34) reduces to

$$\frac{d^2\theta}{d\xi^2}+2\xi\frac{d\theta}{d\xi}=0.$$

The solution is easily seen to be

$$\theta=c\int_0^{\xi}e^{-\xi^2}\,d\xi+\text{const.}$$

Now on a rod, $\theta=\theta_0$ at $x=0$ and $\theta=0$ at $x=\infty$, and at $t=0$, $\theta=0$ everywhere, excepting at $x=0$. These enable us to find out the constants. We have

$$\theta=\theta_0\left\{1-\frac{2}{\sqrt{\pi}}\int_0^{\xi}e^{-\xi^2}\,d\xi\right\}. \qquad (35)$$

The value of the integral will be found in tables.

Now we know θ_0, and we find the value of θ at the point x at the time t. Substituting these values of θ, θ_0 in equation (35) we get the value of the second term inside the curl brackets, viz., the Gaussian error function and then look for the corresponding value of ξ from the table. Knowing ξ we can calculate h from the relation $\xi=\frac{x}{2\sqrt{ht}}$, x and t being already known. This method can be utilised for determining the age of the earth (§14·33).

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[1] *Ann. de Chim. et de phys.*, **66**, 183, 1862.

[2] *Wied. Ann.*, **9**, 1, 1880; **13**, 406, 1881. [3] *Wied. Ann.*, **66**, 207, 1898.

[4] *Ann. d. Physik*, **3**, 43, 1900. [5] *Verh. d. D. Phy. Ges.*, **5**, 60, 1903.

[6] For the method of solving such equations the reader is referred to Carslaw, *The Conduction of Heat*, Chap. III, or Ingersoll and Zobel, *Mathematical Theory of Heat Conduction*, Chap. VII where, many more cases of aperiodic heating are discussed.

14·15. Relation between the Thermal and Electrical Conductivities of Metals : Wiedemann-Franz Law.—A table of thermal conductivities is given on p. 611. The table shows unmistakably that all good conductors of electricity are also good conductors of heat, and even before any theory was proposed, Wiedemann and Franz[1] gave the empirical law that *the ratio of the thermal and electrical conductivities at a particular temperature is the same for all metals.* Lorentz[2] extended the law and showed that this *ratio is proportional to the absolute temperature.*

Drude[3] attempted to explain this remarkable result by assuming that free electrons are responsible for both the thermal and the electrical conduction in metals. He further assumed that the free electrons inside the metal behave like gas molecules and since they collide and are in equilibrium with the atoms of the metal, they will have, from the law of equipartition, the same energy per degree of freedom as the atom inside the metal.

Let us consider the conduction of electricity in a metallic wire. If the electric intensity along the wire is X every electron in the metal is acted on by the force Xe and possesses the acceleration Xe/m, where m is the mass of the electron. Let λ be the mean free path and $\bar{v}$ the mean velocity of the electrons corresponding to the temperature $T°$. The electron is accelerated between two collisions but parts with its acquired velocity on collision with the atom. Thus the velocity at the beginning of the path is zero, that at its end is $\frac{\lambda}{c} \cdot \frac{Xe}{m}$, and hence the average drift velocity u may be put as mean of these two, *i.e.*, $u = \frac{1}{2} \frac{\lambda}{\bar{v}} \frac{Xe}{m}$.

The number of electrons crossing unit area per second is nu where n is the number of free electrons per unit volume. The current per unit area becomes equal to neu. Therefore

$$i = ne. \frac{1}{2} \frac{\lambda}{\bar{v}} \frac{Xe}{m}. \qquad (36)$$

Thus the electrical conductivity σ of unit length and unit cross-sectional area is given by

$$\sigma = \frac{i}{X} = \frac{ne^2\lambda}{2mc} = \frac{ne^2\lambda\bar{v}}{6kT}, \qquad (37)$$

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[1] *Pogg. Ann.*, **89**, 497, 1853.

[2] *Pogg. Ann.*, **147**, 429, 1872.

[3] *Ann. d. Physik*, **1**, 556, 1900.

since $m\bar{c}^2=3kT$, if we neglect the difference between the mean velocity and the square root of the mean square velocity and assume the validity of the equipartition law.

The thermal conductivity K for the electron-gas expressed in calories is (see Chapter III, p. 173)

$$K=\frac{1}{3}\frac{n\bar{\vartheta}\lambda}{J}\cdot\frac{dE}{dT}=\frac{1}{2}\,\frac{n\bar{\vartheta}\lambda}{J}\,k, \quad . \quad . \quad . \quad . \quad (38)$$

since $E=\frac{3}{2}kT$, if the electron is assumed to possess only the translational energy and no rotational or internal energy.

Hence from (37) and (38) we get

$$\frac{K}{\sigma T}=\frac{3}{J}\left(\frac{k}{e}\right)^2=\text{const.} \quad . \quad . \quad . \quad . \quad (39)$$

which gives the laws of both Wiedemann and Franz, and of Lorentz.

The above equation was put to rigid experimental test by various workers especially by Jaeger and Diesselhorst[1] and by Lees.[2] The results show that at ordinary temperatures equation (39) is satisfied for pure metals but at lower temperatures the value of $K/\sigma T$ falls off. In equation (39) K is in calories per cm. per degree and σ in absolute electromagnetic units. Then we have

$$\frac{K}{\sigma T}=\frac{3}{4\cdot2\times10^7}\left(\frac{1\cdot37\times10^{-16}}{1\cdot59\times10^{-20}}\right)^2=5\cdot3.$$

If however K be expressed in watts/cm. × degree and σ in reciprocal ohms, then

$$\frac{K}{\sigma T}=5\cdot3\times4\cdot2\times10^{-9}=2\cdot2\times10^{-8}.$$

The values for $K/\sigma T$ obtained experimentally are given in table 1, p. 593. The values actually found are thus seen to be larger at ordinary temperatures than that given by the law.

The experiments of Meissner[3] and of Onnes and Holst[4] also support the view that the value of $K/\sigma T$ falls with the fall of temperature. Now at low temperatures both the thermal and electrical conductivities are found to increase. Hence it follows that the thermal and the electrical conductivity do not increase in the same

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[1] *Berlin-Sitzungsber*, **38**, 719, 1899.

[2] *Phil. Trans.*, **208**, 381, 1908.

[3] *Ber. deut. phys. Ges.*, **12**, 262, 1914.

[4] *Leiden Commun.*, No. 133 *c* (1913).

Table 1.—*Values of* $(K/\sigma T) \times 10^8$.

Metal	From Lees' experiment				Jaeger and Diesselhorst	
	−170°C.	−100°C.	0°C.	18°C.	18°C.	100°C.
Aluminium ..	1·50	1·81	2·09	2·13	2·19	2·27
Copper ..	1·85	2·17	2·30	2·32	2·29	2·32
Silver ..	2·04	2·29	2·33	2·33	2·36	2·37
Zinc ..	2·20	2·39	2·45	2·43	2·31	2·33
Cadmium ..	2·39	2·43	2·40	2·39	2·43	2·44
Tin ..	2·48	2·51	2·49	2·47	2·53	2·49
Lead ..	2·55	2·54	2·53	2·51	2·46	2·51
Iron ..	3·10	2·98	2·97	2·99	2·76	2·85
Brass ..	2·78	2·54	2·45	2·45	..	..
Manganin ..	5·94	4·16	3·41	3·34	3·14	2·97

ratio as the temperature falls, the electrical conductivity increasing much more rapidly. In fact the latter appears to become infinite for pure metals at the absolute zero but for impure metals it attains a certain limiting value σ_r independent of the temperature. A part of the variation of $K/\sigma T$ with temperature has also to be attributed to the fact that the thermal conductivity of metals is not entirely due to the electrons but takes place by a process similar to heat conduction in insulators.[1]

14·16. Theories of Conductivity.—The free-electron theory of Drude was carried to its logical conclusion by Lorentz[2] who performed an accurate and detailed analysis of the problem from classical statistics. He determined the modification of the Maxwell-Boltzmann distribution law due to the presence of electric field and temperature gradient, and obtained more precise values of the thermal and electrical conductivities. He got 2, instead of 3, in eqn. (39), and the agreement with experimental results thus became worse than in the simple Drude's theory.

The two major objections to the theory, however, were (1) the specific heat difficulty, and (2) the existence of large mean free path at low temperatures.

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[1] See de Haas and de Nobel, *Physica*, 5, 449, 1938.

[2] See H. A. Lorentz, *The Theory of Electrons* (1923) for a discussion of this work

According to the law of equipartition the average energy of the electrons is equal to that of the atoms, but it is found that the atomic heat of conductors and non-conductors is the same, showing that the electrons do not contribute anything to the atomic heat. This difficulty was cleared by Sommerfeld[1] who assumed that the electrons inside the metal behave as a degenerate gas at ordinary temperatures and the distribution of energy amongst the electrons is not given by the Maxwell's law but by the F-D statistics (see Chap. XVII) and hence the contribution to the atomic heat by free electrons comes out to be negligible. Sommerfeld modified Lorentz's treatment by applying Fermi-Dirac statistics instead of classical statistics, and obtained $\pi^2/3$ in place of 2 of Lorentz in eqn. (39), thus getting a better agreement with experimental results.

Many of the outstanding difficulties were solved by the Lorentz-Sommerfeld free-electron theory of metals, but the mean free path difficulty remained. In this model it is difficult to explain the existence of large mean free paths at low temperatures which must evidently occur since the resistance is observed to decrease with decrease of temperature. In fact since resistance vanishes at absolute zero, the electronic mean free path must become infinite. Houston[2] and Bloch[3], discarding the free-electron theory, considered the interaction between electrons and lattice ions of the metal on a quantum-mechanical basis and showed that inelastic electron-lattice collisions are of primary importance in determining the resistance. They showed that in a perfect non-oscillating lattice the mean free path of the electron would be infinite but on account of the thermal oscillations of the lattice the electrons are scattered giving rise to a finite resistance and a finite mean free path which thus varies with temperature. For details of calculation and comparison with experimental results see Seitz, *The Modern Theory of Solids*, Chap. XV. More recent experiments with aluminium, cadmium, iron and other metals show that the thermal conductivity K can be represented by the relation

$$\frac{1}{K}=\frac{A}{T}+BT^2. \quad . \quad . \quad . \qquad (40)$$

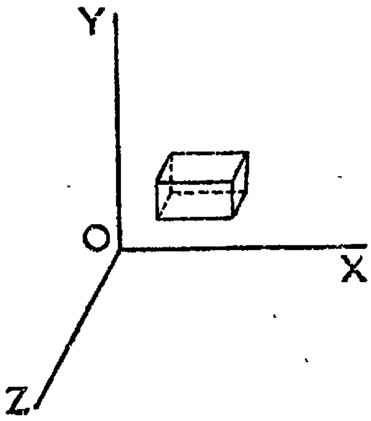

Fig. 13.—Conduction in three dimensions.

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[1] *Zeits. f. Physik*, **47**, 1, 1927; see also *Reviews of Modern Physics*, **3**, 1, 1931, and F. Seitz, *The Modern Theory of Solids*, Chap. IV (1940).

[2] *Zeits. f. Physik*, **48**, 449, 1928.

[3] *Zeits. f. Physik*, **52**, 555, 1928; **59**, 208, 1930.

Such an expression has been theoretically justified by Makinson[1] and by Sondheimer[2]. The first term on the right in (40) is the thermal resistivity due to scattering of the electrons by impurities in the metal while the second term is due to the scattering by the lattice vibrations.

14·17. Heat Conduction in Three Dimensions.—Till now we have considered the flow of heat in one direction only, generally along bars of great length of small width and thickness. We shall now consider the conduction of heat in three dimensions inside an isotropic body. Let us choose three mutually perpendicular axes of reference OX, OY, OZ and consider a small rectangular parallelepiped of edges δx, δy, δz (Fig. 13) and denote the temperature at the centre of the element by θ. The temperature gradient $d\theta/dx$ over this infinitesimal thickness may be assumed constant. Hence the temperature of the inner face is $\theta-\frac{1}{2}\frac{d\theta}{dx}\,\delta x$, that of the outer face is $\theta+\frac{1}{2}\frac{d\theta}{dx}\,\delta x$. The heat flowing in at the inner face per second in the positive direction of x-axis is

$$-K\frac{d}{dx}\left(\theta-\tfrac{1}{2}\frac{d\theta}{dx}\delta x\right)\delta y\,\delta z,$$

and that flowing out at the other face is

$$-K\frac{d}{dx}\left(\theta+\tfrac{1}{2}\frac{d\theta}{dx}\delta x\right)\delta y\,\delta z.$$

Hence the difference equal to

$$K\frac{d^2\theta}{dx^2}\,\delta x\,\delta y\,\delta z$$

remains lodged in that element of volume. Similarly for the propagation of heat along the y and the z axes we get terms

$$K\frac{d^2\theta}{dy^2}\delta x\,\delta y\,\delta z \quad \text{and} \quad K\frac{d^2\theta}{dz^2}\delta x\,\delta y\,\delta z.$$

Hence the total amount of heat lodged in that element is

$$K\left(\frac{d^2\theta}{dx^2}+\frac{d^2\theta}{dy^2}+\frac{d^2\theta}{dz^2}\right)\delta x\,\delta y\,\delta z. \qquad . \quad . \quad . \quad (41)$$

This heat produces a rise of temperature of the element equal to $d\theta/dt$ per second and hence must be equal to

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[1] *Proc. Camb. Phil. Soc.,* **34**, 474, 1938.

[2] *Proc. Roy. Soc. London,* **203**, 75, 1950.

$\rho c. d\theta/dt. \delta x\delta y\delta z$, where ρ is the density of the material and c its specific heat. Therefore

$$K\left(\frac{d^2\theta}{dx^2}+\frac{d^2\theta}{dy^2}+\frac{d^2\theta}{dz^2}\right)=\rho c\frac{d\theta}{dt};$$

or

$$h\nabla^2\theta=\frac{d\theta}{dt}, \qquad \ldots \qquad (42)$$

where h is the diffusivity. This is the Fourier equation of heat conduction in general and we can solve it when the initial conditions are given. The particular case of one-dimensional flow (equation 6) may be obtained from this. Equation (42) is of great importance in studying problems on heat conduction.

CONDUCTIVITY OF POORLY CONDUCTING SOLIDS.

14·18. In finding the conductivity of poor conductors the substance cannot be employed in the form of long bars or rods as was the case with metals, for the heat loss from the sides would be considerable compared with the heat actually conducted away through the substance itself. For this reason, the substance is generally used in the form of a thin plate, sphere or cylinder. To this class belong all non-metallic bodies. Cork, asbestos, clay, wood, bricks, etc., are among the many substances of common occurrence. The conductivity of these varies from 0·01 to 0·00008. We shall now give the important methods of finding the conductivity of these substances.

Some investigators have employed the method of measuring the thermal energy applied to the substance. Among these may be mentioned Peclet, Wologdine[1], Goerens and others. But the method is less common and will not be considered here. In the methods commonly employed for finding conductivity energy is supplied electrically to a separate heating body, and the flow of heat through the experimental substance investigated.

14·19. Spherical Shell Method.—The simplest case of heat conduction in three dimensions is that of a sphere. If the source of heat is placed at the centre of the sphere the isothermal surfaces will be spherical surfaces described about the centre.

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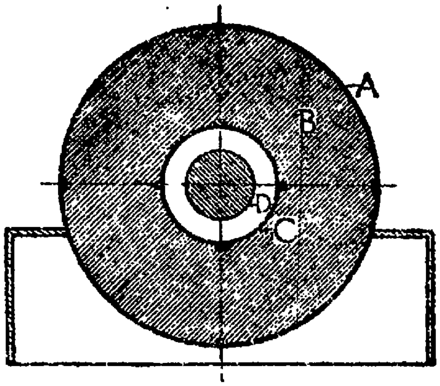
[1] *Rev. de Metallurg.*, 1909, p. 767.

The method was employed by Nusselt[1] and others. Nusselt's apparatus is shown in Fig. 14.



Fig—. 14.—Nusselt's apparatus.

The external hollow sphere A is 30 cm. in diameter and made of copper. Inside it and concentric with it, is another hollow sphere C of aluminium, 15 cm. in diameter. The spheres can be split into two and reunited. The space between the spheres is filled with the material B under test, such as asbestos, powdered cork, charcoal, etc. An electrically heated body D is placed at the centre of the sphere inside C and electrical energy is supplied at a constant rate. Temperatures are determined by means of thermocouples placed in B at different distances from the centre and along one or more radii. Knowing the electrical energy spent and the radii of the shells, the conductivity can be calculated.

We can deduce the equation for this case from the general relation expressed in (42) by replacing x, y, z by a single variable r when we shall get

$$r^2 \frac{d\theta}{dt} = h \frac{d}{dr}\left(r^2 \frac{d\theta}{dr}\right) . \qquad (43)$$

We shall however solve the problem from elementary principles. On account of the symmetry about the centre the isothermal surfaces are spherical. The flux of heat across a spherical surface of radius r outwards in unit time is $-K.4\pi r^2 \frac{d\theta}{dr}$. This must equal the amount of electrical energy Q supplied per second to the heating body. Hence[2]

$$Q = -4\pi K.r^2 \frac{d\theta}{dr} ;$$

or

$$d\theta = -\frac{Q}{4\pi K} \cdot \frac{dr}{r^2} . \qquad (44)$$

Since Q is independent of r we have on integrating (44)

$$\theta = \frac{Q}{4\pi K} \cdot \frac{1}{r} + A, \qquad (45)$$

where A is a constant of integration.

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[1] *Zeits. d. Ver. deutsch Ing.*, **52**, 906, 1908; *Forsch. Ver. d. Ing.*, **63**, and **64**, 1909.

[2] We can also proceed as in Sec. 14.6.

If the two surfaces of the shell of radii r_1, r_2 acquire temperatures θ_1, θ_2 in the steady state, we have

$$\theta_1 = \frac{Q}{4\pi K}\cdot\frac{1}{r_1} + A, \quad \theta_2 = \frac{Q}{4\pi K}\cdot\frac{1}{r_2} + A;$$

whence $$Q = \frac{4\pi K(\theta_1-\theta_2)r_1 r_2}{r_2 - r_1}. \quad . \quad . \quad . \quad (46)$$

Knowing Q, θ_1, θ_2 and r_1, r_2 as in the above experiment the conductivity K can be calculated. Again solving the simultaneous equation for Q and A, and substituting these values of Q and A in (45) the temperature distribution in the material can also be found, and is given by the expression

$$\theta = \frac{1}{r_2 - r_1}\left[(r_2\,\theta_2 - r_1\,\theta_1) + \frac{(\theta_1-\theta_2)r_1 r_2}{r}\right] \quad . \quad . \quad . \quad (47)$$

14·20. Cylindrical Shell Method.—Let us consider the radial flow of heat in a cylinder which has an electrically heated wire along its axis. By suitably transforming equation (42) we can get the equation for this case. We shall, however, as before, deduce it from elementary considerations. Since the cylinder is symmetrical about its axis, the isothermal surfaces are cylindrical. The amount of heat Q flowing per second across such an isothermal surface is

$$Q = -2\pi rl.\,K.\frac{d\theta}{dr}, \quad . \quad . \quad . \quad . \quad (48)$$

where l is the length of the cylinder. Now Q must remain constant, being equal to the electrical energy supplied per second. On integrating between the inner and outer radii of the cylindrical shell with corresponding temperatures θ_1, θ_2, we have

$$2\pi lK(\theta_1 - \theta_2) = Q \log (r_2/r_1),$$

or $$K = \frac{Q}{2\pi l}\cdot\frac{\log_e (r_2/r_1)}{\theta_1 - \theta_2} \quad . \quad . \quad . \quad . \quad . \quad (49)$$

The temperature θ at a distance r can be shown to be given by

$$\theta = \frac{1}{\log_e (r_2/r_1)}\left[(\theta_1 \log r_2 - \theta_2 \log r_1) - (\theta_1 - \theta_2)\log r\right]. \quad . \quad (50)$$

Niven[1] devised a method of determining coductivities based on this principle. The cylinder of the material is formed by filling the space between two hollow concentric cylinders with that material. Heat is supplied by a wire carrying an electric current along the axis of the cylinder, and when the steady state is reached, temperatures at two points within the material are observed as well as their distances from the axis. Knowing the electrical energy spent, equation (49) gives the conductivity.

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[1] *Proc. Roy. Soc. Lond.*, **76**, 34, 1905.

The method was employed by Clement and Egy[1], and Rinsum.[2] Rinsum took into account several corrections, such as the flow of heat along the tube by conduction, etc. A modified form of apparatus has been employed by Stephens[3] in which a hollow cylinder made of the experimental substance is immersed in a constant temperature liquid bath. The rate of rise of temperature of a mass of liquid contained in the cylinder is observed. From this the conductivity could be calculated.

A simple laboratory experiment based on this method may be devised for finding the conductivity of rubber and glass in the form of a tube. For rubber the arrangement shown in Fig. 15 is most convenient. Steam from the boiler A traverses through a rubber tube B, a length l of which is immersed in a weighed amount of water contained in the calorimeter C. The radial flow of heat Q from the tube to the water in C is given by

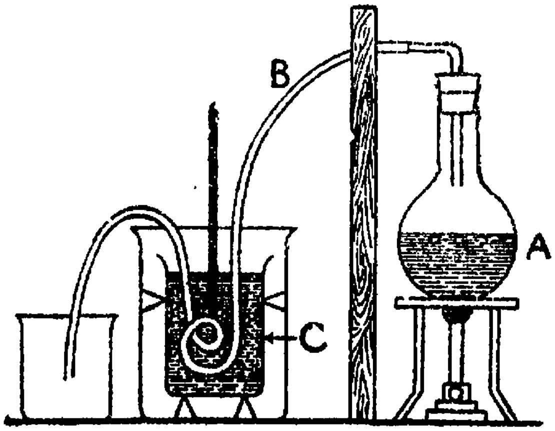

Fig. 15.—Apparatus for finding conductivity of rubber.

$$Q = \frac{2\pi K l(\theta_1 - \theta_2)}{\log_e (r_2/r_1)}, \quad . \quad . \quad . \quad . \quad . \quad (51)$$

where θ_1 represents the temperature of steam, and θ_2 the mean of the initial and final temperatures of the calorimeter. This heat can be calculated from the rise in temperature of the calorimeter and its thermal capacity and hence equating these two quantities we get K, provided r_1, r_2 are known.[4]

For glass the arrangement shown in Fig. 16 is convenient. The glass tube C has a spiral wire along its axis and is surrounded by a steam jacket, while a steady current of water flows through the tube. The method of calculation is similar to the preceding one.

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[1] *Phys. Rev.*, **28**, 71, 1909.

[2] *Forschungsarbeiten Ver. d. Ing.*, **228**, (1920).

[3] *Phil. Mag.*, **15**, 857, 1933.

[4] For experimental details see Worsnop and Flint, *Practical Physics*.

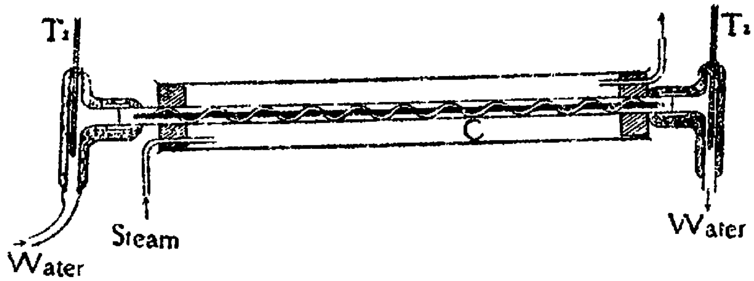

Fig. 16.—Apparatus for finding conductivity of glass.

14·21. Disc Method.—This method is most suitable for finding the conductivity of substances which can be had in the form of a disc or plate. It was first given by Lees.[1] An improved apparatus employed by Poensgen[2] is shown in Fig. 17. P_1, P_2 are two similar plates of the substance to be investigated. H_p is a square-sized plate heated electrically and surrounded completely on all sides by H_r which is also made of the same material. K_1, K_2 are two plates which are cooled by water and are separated from the plate by bolts. The whole is enclosed in a chest K filled with badly conducting substance (cork-shavings, etc.). The temperatures θ_1, θ_2 of the heating body and the cold plates respectively are measured by thermo-elements fixed to the surfaces. The temperatures of H_p and H_r can be kept equal by regulating the electric current. The flow of heat from H_p is now quite perpendicular to the plates P_1 and P_2, the radial loss of heat being prevented by the guard-ring H_r. The conductivity is given by the formula

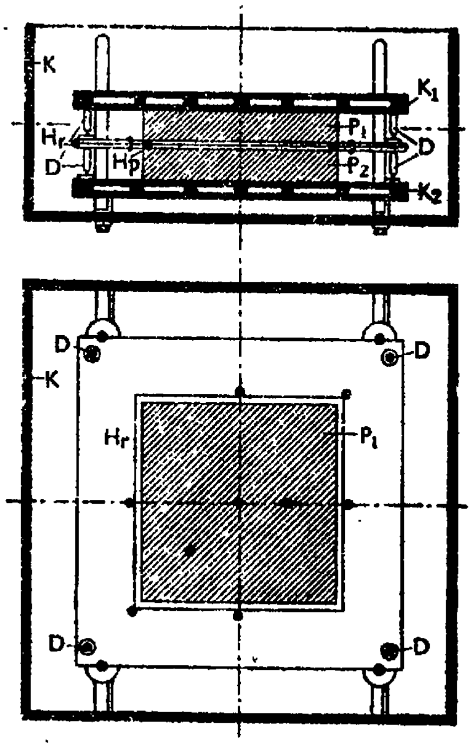

Fig. 17.—Poensgen's apparatus for finding conductivity by Disc Method.

$$K = \frac{Ql}{2A(\theta_1-\theta_2)t}, \quad . \quad . \quad . \quad (52)$$

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[1] *Mem. and Proc. Manchester Soc.*, Vol. **43**, 3, No. 8 (1898-99).

[2] *Forschungsarbeiten, herausgeg, Ver. d. Ing.*, **130**, 25, 1912; *Zeits. d. Ver. d. Ing.*, **56**, 1653, 1912.

where Q is the amount of heat added in time t, l is the thickness and A the area of the plates P_1 or P_2. The method is very suitable for the investigation of conductivity of badly conducting substances particularly of materials used in buildings.

Jakob[1] has modified the apparatus in which only one plate is used. For details see *Handbuch der Physik*, Vol. XI, p. 106.

The divided bar method, explained in §14·23 has also been employed by several workers with good results.

The periodic heat-flow method has been employed by Heyn, Honda and Sato and by Tadokoro,[2] but is less common.

CONDUCTIVITY OF CRYSTALS.

14·22. Senarmont's Work.—We have so far considered isotropic bodies for which the conductivity is the same in all directions. But the conductivity of crystalline and anisotropic bodies is different in different directions. Thus Tyndal found by Despretz's method that the conductivity of wood was greatest along the fibre and least in the direction perpendicular to the fibre and the ligneous layers. Jannettaz found for laminated rocks that the conductivity was best parallel to the planes of cleavage and worst perpendicular to them.

The first systematic and extensive investigation of the conductivity of crystals was carried out by De Senarmont.[3] A thin plate with parallel faces was cut from the crystal in any desired direction and the two faces were thinly coated with wax. Heat was applied at one point in the plate in any of the following ways. Either the sun's rays were concentrated by a short focus lens to a point on the surface of the plate or a wire passed through a hole in the plate and was heated electrically. In some experiments a fine silver tube passed through the hole and was heated by a flame. As portions of the plate became heated the wax on them melted. Finally in the steady state the bounding line of the melted wax represents an isothermal line corresponding to the temperature of melting point of wax. The conductivity in different directions can be calculated from the lengths along which the wax melts, much in the same way as in Ingen-Hausz's experiment.

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[1] *Zeits. d. Ver. Ing.*, **66**, 688, 1922; *Zeits. f. Instrkde.*, **44**, 108, 1924.

[2] *Sci. Reports, Tohoku Univ.*, **10**, 339, 1921.

[3] *Ann. de Chimie et de Physique*, 3e, **21**, **22**, **23**, (1847-48).

Senarmont obtained very interesting results. For isotropic substances, such as glass and cubic crystals, the isothermal curve was always a circle, while for other crystals in general it was an ellipse. The isothermal surfaces round the heated point were in general a system of concentric triaxial ellipsoids. The axes of these ellipsoids which are called the *thermic axes* of the crystal coincided with the crystallographic axes of symmetry in case of a very symmetrical crystal. In the rhombohedral system the isothermal surface is an ellipsoid of revolution about the axis of the crystal which is the only axis of symmetry. For these the isothermal curves were found to be circles in plates cut perpendicular to the axis and ellipses in plates cut parallel to the axis. Fig. 18 shows such curves for a quartz crystal cut perpendicular and parallel to the axis. The rule was found to hold for all crystals. Later experiments confirmed these conclusions. A theory of conduction of heat in crystals was given by Stokes[1] which explains completely the results of experiments. For details see the original papers.

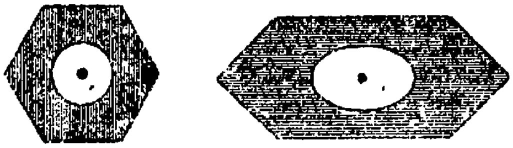

Fig. 18.—Isothermal surface in quartz cut (1) perpendicular (2) parallel to the axis.

14·23. Absolute Conductivity of Crystals.—The absolute conductivity of crystals was investigated by Lees by a method suggested by Lodge. A thin plate of the crystal was joined at both of its faces to brass rods of the same cross-section. One end of this compound or divided bar was heated by steam and the other cooled by water. Tempreatures were measured at several points along the bar by means of thermo-couples and thereby the temperature of the two faces of the crystal was known. If the conductivity of brass is known, the conductivity of the crystal can be easily calculated.

Eucken[2] used a modification of Less' disc method. Tbe crystal was placed between two plates of copper, the lower one of which was heated by a known amount of electrical energy supplied to a wire wound on it. The lower plate rested on pine wood supports and it was so arranged that nearly all the heat flowed upwards through the crystal. Knowing the electrical energy spent and the temperature distribution the conductivity can be calculated. Corrections must be applied for loss due to radiation and conduction through the pine wood.

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[1] G. G. Stokes, *Collected Papers*, Vol. 3, p. 203, or see Preston, *Theory of Heat*, pp. 671—676.

[2] *Ann. d. Physik*, **34**, 185, 1911.

Eucken's experiments[1] were carried down to —252°C. He discovered an important law, *viz.*, *the thermal conductivity of these crystals is inversely proportional to the absolute temperature.* A theoretical explanation of this result was given by Debye[2] who worked out the kinetic theory of the transfer of heat in dielectric solids by considering it as a propagation of elastic waves in a continuous medium. These waves were regarded as scattered by a stationary system of density variations in the solid produced by the whole set of waves. Pauli[3] showed that the atomic nature of the solid lattice must be taken into account when the scattering centres move with the same order of velocity as the waves themselves and Peierls[4] worked out the theory for this case and showed that the thermal conductivity of a crystal lattice will increase with decreasing temperature. For a crystal of finite size at sufficiently low temperatures the free path of the elastic waves becomes comparable with the dimensions of the crystal and then effects due to scattering of the waves at the boundaries will increase the resistance to the flow of heat. Casimir[5] has shown that the resistance due to scattering at the boundaries will produce a thermal resistance varying as T^3 which he confirmed from the experimental measurements of de Haas and Biermasz[6] in the range 2 to 4 °K.

CONDUCTIVITY OF LIQUIDS

The determination of the conductivity of a liquid is complicated by the presence of convection currents. If we heat a column of liquid at the bottom, the liquid at the top receives heat both by conduction and convection. The laws governing convection currents are complicated, hence it is preferable to eliminate them. This is accomplished either by taking a column of liquid and heating it at the top, or by taking a thin film of liquid.

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[1] *Verh. d. D. Phys. Ges.*, **13**, 829, 1911; *Phys. Zeits.*, **12**, 1005, 1911.

[2] *Debye, Wolfskehl-Vorträge zu Göttingen*, Leipzig, 1914.

[3] *Verh. d. deuts. phys. Ges.*, **6**, 10, 1925.

[4] *Ann. d. Physik*, **3**, 1055, 1929. [5] *Physica*, 5, 495, 1938.

[6] *Physica*, **5**, 320, 619, 1938.

14·24. Column Method.—The column method was employed by Despretz long ago. The liquid at the top was kept heated and temperatures along the axis of the column were observed by mercury thermometers. He found that Fourier's equation already derived for a bar holds true in this case also, and hence the conductivities of two liquids can be compared with the help of equation (11). Weber[1] surrounded the column with a guard-ring and used as the source of heat an electrically heated oil bath. The bottom of the column was cooled by a copper plate standing in ice. The heat conducted away was found from the amount of ice melted. Knowing the temperature distribution along the column the absolute conductivity can be calculated in the same manner as for mercury in Berget's experiment.

14·25. Film Method.—This was employed by Lees,[2] Milner and Chattock[3] and by Jakob.[4] We shall describe the apparatus used by Lees, which is simply a modification of his disc method for finding the conductivity of poor conductors. The liquid L under test is enclosed in an ebonite ring E (Fig. 19) and placed between copper blocks C_1, C_2. To determine the quantity of heat flowing through the liquid a glass disc G is inserted above which another copper plate C_3 is cemented with a layer of shellac. Above C_3 and insulated from it by mica is placed a flat spiral coil of heating wire W which is held down by another copper plate C. The whole pile is varnished and enclosed in an air-bath. Temperatures are recorded by thermocouples soldered to the faces of the copper plate. The calculations can be easily made.

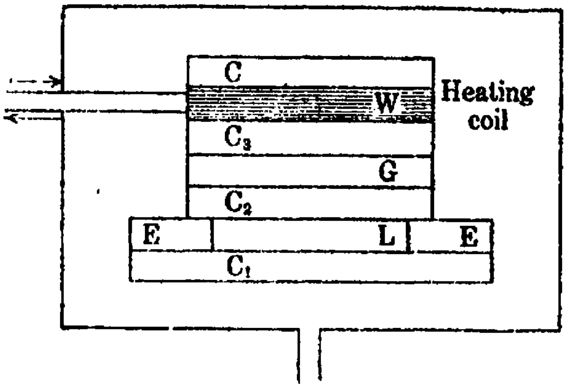

Fig. 19.—Lees' apparatus for finding conductivity of liquids.

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[1] *Ann. d. Physik*, **11**, 1047, 1903.

[2] *Phil. Trans.*, **191**, 418, 1898.

[3] *Phil. Mag.*, **48**, 46, 1899.

[4] *Ann. d. Physik*, **63**, 537, 1920.

Let S_1, S_2, S_2, S_G denote the emitting surfaces of C_1, C_2, C_3, and G respectively, h their emissivity and T_1, T_2, T_3, the temperatures of the copper discs. If the heat leaving the lower surface of G is Q, that entering the upper surface must be

$$Q+S_G\, h\, \frac{T_3+T_2}{2}.$$

The heat passing through the glass disc may be put equal to the mean of the heat entering and leaving it. Hence the heat passing through it is

$$Q+S_G\, h\, \frac{T_3+T_2}{4},$$

and this must equal

$$AK_G\, \frac{T_3-T_2}{d_G}.$$

Hence the heat leaving the lower surface of G is

$$Q = AK_G\, \frac{T_3-T_2}{d_G} - S_G\, h \frac{T_3+T_2}{4}.$$

Of this an amount $T_2S_2\, h$ is lost by radiation from the sides of C_2 and the remainder, *viz.*,

$$Q_2 = AK_G\, \frac{T_3-T_2}{d_G} - S_G\, h \frac{T_3+T_2}{4} - T_2S_2h, \quad . \qquad (53)$$

is transmitted through the liquid and the ebonite. The heat transmitted through the liquid is $K_L A_L\, (T_2-T_1)/d_L$, and that through the ebonite may be put equal to $B(T_2-T_1)$, where the suffix L stands for the liquid, and B is some constant.

$$\therefore\ Q_2 = K_L\, A_L \frac{T_2-T_1}{d_L} + B(T_3-T_1). \quad . \quad . \qquad (54)$$

The constant B can be determined by performing an experiment in which the liquid was replaced by air whose conductivity was known. Then the above expression gives K_L, the conductivity of the liquid, since other quantities involved there are determinate.

14·26. *Hot-Wire Method.*—Goldschmidt[1] employed the "hot-wire" method of Andrews and Schleiermacher, the theory of which is discussed in §14·20. The liquid was contained in a silver capillary tube 2 mm. in diameter and heated by a wire running along its axis.

Coaxial Cylinder Method.—The liquid is here enclosed in the annular space between two concentric cylinders. The method was used by Winkelmann[2] who placed the concentric cylinders in a water-bath and observed the rate of change of temperature inside the internal cylinder.

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[1] *Phys. Zeits.*, **12**, 417, 1911. [2] *Pogg. Ann.*, **153**, 481, 1874.

Bridgman[1] supplied the heat energy by means of an electrically heated wire passing along the axis of the cylinders and observed the temperatures at the surfaces of the two cylinders. He investigated the variation of conductivity with pressure.

Flow Methods.—Graetz first employed the flow method. Callendar[2] however devised a better apparatus. A long platinum tube was heated electrically by a current and a continuous stream of liquid was allowed to flow through it. Knowing the rate of flow of the liquid and the temperature gradient along the tube as well as the temperatures at the surface and on the axis of the tube, the conductivity could be calculated. For details see the original papers.

Nettleton[3] forced a slow stream of mercury up a vertical glass tube whose top was heated by steam and bottom cooled by ice. The middle part of the tube was surrounded by a constant temperature bath.

CONDUCTIVITY OF GASES

14·27. The determination of the conductivity of gases is difficult for it is so small that it is generally masked to a large extent by the accompanying radiation and sometimes convection also. Kundt and Warburg[4] found that the rate of cooling of a thermometer immersed in air remained constant for pressures lying between 150 mm. and 1 mm. They concluded that loss of heat by convection was negligible in this region, and heat is lost only by conduction and radiation. To determine the radiation loss, the air was exhausted as completely as possible, and then the rate of cooling was found to be independent of the size of the enclosure, showing that the effect of conduction was negligible and heat was lost only by radiation. Subtracting this radiation loss, we get the heat lost by conduction alone. For finding the conductivity of a gas at pressures higher than 150 mm. the gas may be exhausted to this pressure (between 150 mm. and 1 mm.) and its conductivity determined. Now since the conductivity of a gas is independent of the pressure (see Chapter III, Sec. 3·39) this will give the required conductivity. Another procedure consists in taking a thin film of gas and heating it at the top when convection will be absent.

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[1] *Proc. Amer. Acad.*, **59**, 140, 1923.

[2] *Phil. Trans.*, **199**, 110, 1902.

[3] *Phil. Mag.* **19**, 587, 1910; *Proc. Phys. Soc.*, **22**, 1910; **25**, 1913.

[4] *Pogg. Ann.*, Vols. 155 and 156; *Jour. de Physique*, **5**, 118, 1876.

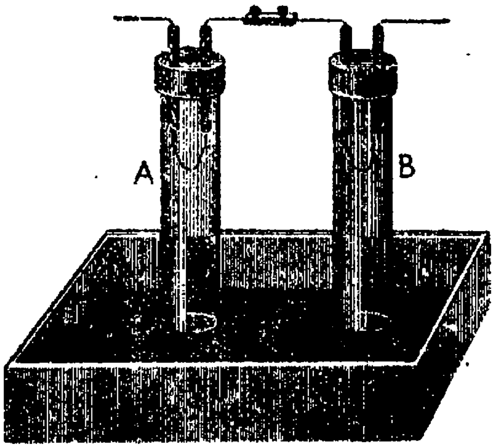

Fig. 20.—Apparatus to show the better conductivity of hydrogen.

A very simple experiment described by Andrews[1] and Grove[2] shows qualitatively that hydrogen is a far better conductor of heat than any other gas. A fine platinum wire was supported inside a glass tube (Fig. 20) which could be filled with any gas. The wire could be heated by an electric current and made to glow. Two such tubes were arranged side by side, one filled with air and the other with hydrogen. The same electric current was allowed to flow through both the wires. The wire in the air-tube can be seen glowing while the wire in the hydrogen tube does not glow at all. The glass tube containing hydrogen also becomes hot. Heat is very quickly conducted away by hydrogen and hence the wire is not raised to the temperature of incandescence. Replacing hydrogen with air restores the incandescence.

The different methods[3] of finding the absolute conductivity of a gas are the following :—

(1) Hot-wire Method, (2) Cooling Thermometer Method, (3) Film Method.

14·28. Hot-wire Method.—This method, first given by Andrews, was employed by Schleiermacher[4] for determining the absolute conductivity of a gas. An electrically heated wire is surrounded by a coaxial cylinder of glass or metal, which is filled with the experimental gas. The temperature of the wire is known from its resistance, and the amount of heat flowing across the curved surface of the cylinder is found from the rate of energy supplied to the wire. Convection and radiation effects are eliminated as pointed out in Sec. 14·27. The conductivity can be calculated from equation (49) where r_1, r_2 now denote the radii of the wire and the tube respectively.

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[1] *Proc. Roy. Irish Academy*, **1**, 465, 1840.

[2] Grove, "*Bakerian Lecture*," *Phil. Trans.* 1847; *Phil. Mag.*, Vol. 27, p. 445.

[3] For a summary of the methods, see Trautz and Zundel, *Zeits. f. techn. Physik*, **12**, 273, 1931.

[4] *Wied. Ann.*, **34**, 623, 1888.

Weber[1] improved the apparatus and considered the various corrections more fully. The lateral heat transfer through the gas is radial only for a limited central portion of the tube and the principal correction to be applied is for the heat conducted longitudinally by the wire. To minimise this a long thin wire is used and the resistance of the central isothermal portion of the wire is measured by attaching two very fine potential leads to the wire. In this way Taylor and Johnston[2] determined accurately the thermal conductivity of a number of gases. Kannuluik and Martin,[3] however, employed a thick wire and corrected for the end effect almost exactly by a rigorous application of the theory. Corrections have also to be applied for the temperature gradient across the wall of the cylinder, for the temperature jump effect (p. 214) at the surfaces of the wire and the tube and for the heat lost by radiation, etc. For full details the original papers may be consulted.

Gregory and Archer[4] employed two tubes, one long and the other short but otherwise identical, usually called compensating cells. The differential measurements then refer to the central portion of the longer tube, where radial flow conditions hold.

This method has been utilised by Senftleben[5] and his pupils for studying a number of physico-chemical reactions amongst which may be mentioned the determination of the percentage of H_2 gas atomised by Franck and Cario's[6] method. Atomic hydrogen has greater conductivity than the molecular species, hence a measurement of the change in conductivity of the gas subject to Franck and Cario's treatment gives the percentage of molecules atomised. Later he also measured by the same method the change of thermal conductivity of paramagnetic gases like O_2, NO when these are placed in a magnetic field. In this case according to the quantum theory these molecules, having a definite magnetic moment, are expected to be oriented along certain definite directions as in Stern and Gerlach's experiment. The conductivity was therefore expected to change. Senftleben found experimentally that the thermal conductivity of paramagnetic gases is reduced by the action of magnetic fields, the effect depending, upto a limit, upon the pressure and temperature of the gas and the field strength. He found empirically that the decrease $-\Delta K$ in conductivity can be expressed by the relation

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[1] *Ann. d. Physik.*, **34**, pp. 325, 437, 481, 1917.

[2] *J. Chem. Phys.*, **14**, 219, 1946.

[3] *Proc. Roy. Soc.*, **144**, 496, 1934.

[4] *Proc. Roy. Soc.*, **110**, 91, 1926.

[5] *Phys. Zeits.*, **31**, 822, 691, 1930; *Ann. d. Physik*, **16**, 907, 1933.

[6] See Ruark and Urey, *Atoms, Molecules and Quanta*, p. 508 (1930).

$$\epsilon = -\frac{\Delta K}{K} = \frac{ax^2}{1+bx+cx^2},$$

where

$$x = H\sqrt{T}/p.$$

As the formula shows, at first ϵ varies with H in a parabolic fashion, then ϵ changes linearly, and ultimately a saturation value is obtained. The exponent of T varies between $\frac{1}{2}$ and 1.

14·29. Cooling Thermometer Method.—This method was employed by Kundt and Warburg.[1] They observed the rate of cooling of a thermometer when its bulb was placed in an enclosure filled with the gas under test. The convection effect was eliminated and radiation effect determined as described above. Then knowing the thermal capacity of the bulb, the conductivity of the gas can be deduced.

14·30. Film Method.—The film method, originally used by Todd[2], has been employed by Hercus and Laby[3]. The principle underlying it is the same as in Lees' experiments (Sec. 14·25). The thin film of gas under test was enclosed between two copper plates B and C (Fig. 21), the latter of which was cooled by a current of water. The upper plate B was made up of two sheets of copper clamped together with a heating coil between them. To prevent loss of heat by radiation from the upper surface of B, there was another plate A above it at the same temperature and a guard-ring D surrounding it. All the plates A, B, D contained separate heating coils and thermocouples and were kept at the same temperature. The whole apparatus was made air-tight. The temperature of A was

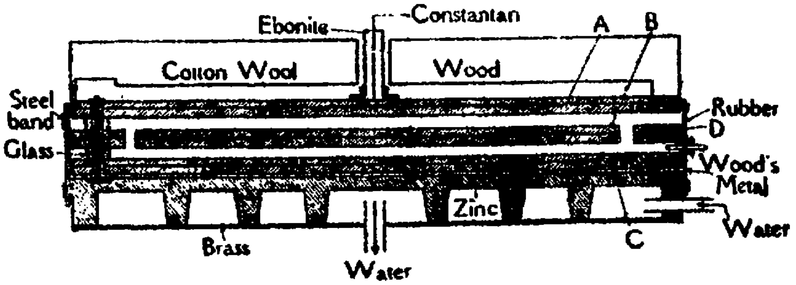

Fig. 21.—Apparatus of Hercus and Laby.

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[1] *Pogg. Ann.* Vols, **155, 156**; *Jour. de Physique*, **5**, 118, 1876.

[2] *Proc. Roy. Soc. Lond.*, **83**, 19, 1909.

[3] *Proc. Roy. Soc. Lond.*, **95**, 190, 1918; see also Hercus and Sutherland, *Proc. Roy. Soc.*, **145**, 599, 1934.

generally kept a little above that of B in order to eliminate any possibility of convection. This however necessitated a small correction. The radiation correction was determined by a separate experiment on a silvered Dewar flask and was very small. Convection effects are entirely absent since the gas is heated at the top. The energy spent in B was known electrically and subtracting from it the heat lost by radiation, the heat transmitted to C by conduction through the air film was found. Knowing the temperature of C the conductivity of the gas can be calculated from equation (4).

14·31. Results.—The thermal conductivity of a number of substances is given in table 2. The value of K is given in calorie cm.$^{-1}$ sec.$^{-1}$ degree^{-1}.

Table[1] 2.—*Thermal Conductivity of different substances.*

Substance	Conductivity	Substance	Conductivity
Metals (0°C)		Asbestos paper ..	$0\cdot6\times10^{-3}$
		Cardboard ..	0·5
Aluminium ..	0·48	Cork ($\rho = \cdot16$) ..	0·11
Cadmium ..	0·23	Paper ..	0·3
Copper ..	0·93	Ebonite ..	0·42
Iron (pure) ..	0·16	Mica ..	1·8
Lead ..	0·085	Paraffin wax ..	0·6
Mercury ..	0·025	Pine wood ..	0·4
Nickel ..	0·14	Rubber ..	0·45
Silver ..	1·0		
Platinum ..	0·17	*Liquids*	
Tin ..	0·155		
Zinc ..	0·265	Water (20°) ..	$14\cdot3\times10^{-4}$
		Alcohol (25°) ..	4·3
Alloys (0°C.)		Glycerine (25°) ..	6·8
Brass ..	0·23		
Constantan ..	0·05	*Gases* (0°C.)	
Manganin ..	0·05		
German silver ..	0·06	Hydrogen ..	$31\cdot8\times10^{-5}$
		Helium ..	33·9
Poor Conducting Solids (18°C)		Argon ..	3·89
		Air ..	5·40
Crown glass ..	$2\cdot5\times10^{-3}$	Oxygen ..	5·63
Flint glass ..	2	Carbon dioxide ..	3·07

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[1] Taken partly from Landolt and Bornstein, *Physikalisch-Chemischen Tabellen* and partly from Kaye and Laby, *Tables of Physical and Chemical Constants.*

Relation between Thermal Conductivity and Viscosity of Gases.—We have already shown in §3·39 that the thermal conductivity K and coefficient of viscosity η of a gas are connected by the relation

$$K = \epsilon \eta c_v$$

where c_v is the specific heat of the gas at constant volume and ϵ a constant equal to $\frac{1}{4}(9\gamma - 5)$, γ being the ratio c_p/c_v. This relation is very important and agrees with experimental results (p. 175)

Variation of Conductivity with Pressure.—Again since for gases $K = \epsilon \eta c_v$, and the variation of c_v is small, while η is independent of pressure except at very high and very low pressures (p. 170), it follows that the thermal conductivity of a gas is independent of the pressure over a wide range. This was experimentally verified by Stefan[1] and others.

14·32. Temperature Variation of Conductivity.—An expression for the variation of thermal conductivity of gases with temperature is obtained from the kinetic theory. Sutherland's expression (p. 172) for the variation of viscosity with temperature should also hold for the conductivity of a gas. This has also been shown by Eucken[2] who finds that for several gases the ratio of the conductivity to the viscosity is constant for temperatures lying between $-80°$C. and $100°$C. This would give, for the variation of conductivity, the expression

$$K_T = K_0 \frac{b + 273}{b + T} \left(\frac{T}{273}\right)^{3/2},$$

which agrees only approximately with experimental results.

14·33. Some Practical Applications[3].—The phenomenon of heat conduction has got various important applications which are treated in works on General Physics and Engineering. Only a few of them are given here.

(*i*) Equation (1) is of great help in the construction of cold storage, furnace, boiler, etc. As an example consider the flow of heat through the walls of any chamber. If the walls have a total area of 1000 sq. metres and conductivity 0·00057 (granite) and are 30 cm. thick, while the temperatures inside and outside are 0° and 30°C. the amount of heat entering the ice chamber per second from outside is

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[1] *Sitzb. Akad. Wiss. Wien.*, **65**, pp. 2, 45, 1872.

[2] *Phys. Zeits.*, **12**, 1101, 1911; **14**, 324, 1913.

[3] A very good account of the various applications of heat conduction is given in Ingersoll and Zobel, *Mathematical Theory of Heat Conduction*.

$$\frac{0{\cdot}00057\times 30}{30}\times 1000 = 0{\cdot}57 \text{ cal.}$$

which will melt ice at the rate of 25 grams per hour.

If the wall is made up of a number of materials of thickness x_1, x_2 and conductivities K_1, K_2 joined together, the amount of heat Q flowing per second per unit area becomes

$$Q = \frac{\theta_1-\theta_2}{\dfrac{x_1}{K_1}} = \frac{\theta_2-\theta_3}{\dfrac{x_2}{K_2}} = \ldots\ldots,$$

where θ_1, θ_2 are the temperatures of the intermediate surfaces. If θ_1, θ_n are the temperatures of the extreme ends

$$Q = \frac{\theta_1-\theta_n}{\left(\dfrac{x_1}{K_1}+\dfrac{x_2}{K_2}+\ldots\right)}. \qquad (55)$$

Hence the heat flowing through the composite wall can be easily calculated.

(*ii*) *Conductivity of the Earth's Crust, Underground Temperatures.*—The periodic flow method (Sec. 14·12) is very suitable for finding the conductivity of the earth's crust. The earth's surface is heated by day and cooled by night. This alternate heating and cooling travels into the interior of the earth in the form of a heat wave (*diurnal wave*) and gives rise to the diurnal variations in temperature inside the earth's crust. Again the earth receives a larger amount of heat in summer than in winter and this causes a second heat wave having the period of one year (*annual wave*) which is also propagated into the interior of the earth. Assuming the waves to be simple harmonic as a first approximation (the annual wave in particular departs considerably from this ideal state), let us find how they progress into the earth. The problem is that of an infinite wall heated and cooled at one end, or that of a bar periodically heated and cooled at one end and provided with a guard-ring. The solution of the problem is given by equations (23) to (30). Now if a number of thermometers are embedded in the earth at different depths the progress of the temperature wave inside the earth can be investigated. Knowing the wavelength, the diffusivity can be calculated from (29), *viz.*,

$$h = \frac{\lambda^2}{4\pi T}.$$

The same treatment can be utilized for solving the geological problem, *viz.*, the penetration of the daily and annual changes of temperature within the earth's crust. From p. 587 the fluctuation of temperature at any point is given by

$$\theta = \theta_0\, e^{-x\sqrt{\pi/hT}} \sin\left(\frac{2\pi t}{T} - x\sqrt{\frac{\pi}{hT}}\right), \quad . \quad . \quad . \quad (27a)$$

when the temperature fluctuation at $x = 0$ is given by

$$\theta = \theta_0 \sin 2\pi t/T.$$

Hence the range of amplitude R at any point x is

$$R = 2\theta_0 e^{-x\sqrt{\pi/hT}}, \quad . \quad . \quad . \quad . \quad . \quad (56)$$

the velocity of propagation

$$V = 2\sqrt{\pi h/T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (57)$$

and wavelength

$$\lambda = 2\sqrt{\pi h T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

The "lag", *i.e.*, the time t which any temperature applied at the surface takes to travel to a point x is given by

$$t = \frac{x}{V} = \frac{x}{2}\sqrt{\frac{T}{\pi h}}. \quad . \quad . \quad . \quad . \quad . \quad (59)$$

We shall now apply these results to the propagation of heat inside the earth's crust. For the daily wave T=24 hours=86400 sec. Taking h=0·0049, the value for ordinary moist soil, we have

$$\lambda = 73\text{ cm.};\ V = 8\cdot4\times10^{-4}\text{ cm./sec};\ \alpha = 1/11\cdot6.$$

Supposing the maximum temperature is 45°C. at 2 P. M. and the minimum is 25°C. just after sunrise, the amplitude of temperature variation being 20°C. This variation will diminish as $e^{-x/11\cdot6}$ at a depth x. For x=10, $e^{-x/11\cdot6} = \cdot42$, for x=30, $e^{-x/11\cdot6} = \cdot076$, for x=100, $e^{-x/11\cdot6} = \cdot00018$. Thus at a depth of 1 metre the temperature variations will be scarcely noticeable.

The slow velocity of penetration of the daily heat wave must have been familiar to all observant minds in a tropical country. Here the house-roofs are exposed to the scorching heat of the sun and at 2 P. M. the temperature may be as great as 60°C. But this temperature travels inward at the extremely slow rate of $9\cdot1\times10^{-4}$ cm./sec. or 6·4 cm. per hour in a mass of concrete.[1] Hence to penetrate a wall depth of 30 to 40 cm. which is the usual thickness of walls, a period of 5 to 6 hours is needed. The inside of the room, provided the windows are shut, therefore reaches its maximum temperature at about 7 or 8 P. M. when the walls become intolerably hot and begin to radiate. Most people must have experienced that it is found impossible to sleep indoors at this time. The minimum at the top of the room is reached at about sunrise. So the rooms are found to be cool from 11 A. M. to about 2 P. M. when the outside is blazing with heat.

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[1] For concrete h may be taken to be 0·0058.

Annual wave.—Besides the diurnal fluctuations the surface of the earth is also subject to an annual period of 365¼ days owing to the different amount of surface heating in winter and in summer. This amount is variable in different countries, but in desert countries it may amount to as much as 60°C. in the sun in summer and 0°C. in winter.

In the case of the annual wave

$$\lambda=73\sqrt{365/1}=73\times19\cdot1=14 \text{ metres.}$$

$$V=8\cdot4\times10^{-4}\sqrt{1/365}=4\cdot5\times10^{-5} \text{ cm./sec.}$$

$$=3\cdot9 \text{ cm. per day.}$$

$$\alpha=\frac{1}{11\cdot6}\sqrt{\frac{1}{365}}=\frac{1}{220}.$$

Thus the annual wave will penetrate a depth of about 1·2 metres in a month. At a depth of $x=\lambda/2=7$ m. the times of the year are interchanged. The amplitude of temperature variation will be reduced by the fraction $e^{-100/220}=\cdot64$ at 1 metre depth and by $e^{-1000/220}=\cdot011$ at 10 metres depth. Thus the annual wave is able to penetrate to a depth which is $\sqrt{365/1}$ = about 19 times greater than the daily wave. Most of these conclusions have been verified experimentally.[1]

(*iii*) *Age of the Earth.*—From the geological point of view the age of the earth is counted from the time when its surface had cooled to a state of sufficient solidity from the fluid *magma*. Corresponding to this all-fluid state, Kelvin assumed a temperature of 3900°C. throughout. He made an estimate of the age of the earth from its conductivity and the present temperature gradient on its surface. The problem is to find how the earth would take to cool from its initial temperature θ_0 for the present geothermal gradient to be attained, its surface being kept constantly at a temperature of 0°C. approximately. The equation is

$$\frac{d\theta}{dt}=h\frac{d^2\theta}{dx^2},$$

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[1] MacDougal, *Monthly Weather Review*, **31**, 375, 1903; *Tamura*, *Ibid.*, **33**, 269, 1905; Rambaut, *Phil. Trans.*, **195**, 235, 1901.

with the boundary conditions

$$x=0,\ \theta=0;\ x=\infty,\ \theta=\theta_0;\ t=0,\ \theta=\theta_0.$$

The solution, as on p. 590, is given by

$$\theta = \theta_0 \frac{2}{\sqrt{\pi}} \int_0^{\xi} e^{-\xi^2} d\xi \ , \qquad \qquad (60)$$

where θ is the temperature at any point and $\xi = \dfrac{x}{2\sqrt{ht}}$ ·

On differentiation

$$\frac{d\theta}{dx} = \frac{\theta_0}{\sqrt{\pi h t}} e^{-x^2/4ht} \qquad \qquad (61)$$

and at $x=0$,

$$\left(\frac{d\theta}{dx}\right)_0 = \frac{\theta_0}{\sqrt{\pi h t}};$$

whence

$$t = \frac{\theta_0^2}{\pi h \left(\dfrac{d\theta}{dx}\right)_0^2}. \qquad \qquad (62)$$

Kelvin put $\theta_0 = 3900°\text{C}$, $h = 0{\cdot}01178$, $\left(\dfrac{d\theta}{dx}\right)_0 = \dfrac{1}{2776}$ and got a value of 100 million years for the age of the earth. Even allowing much possibility of error in the assumed values, this estimate falls short of the value given by geologists. This is due to the presence of radioactive bodies inside the earth, which continuously generate a large amount of heat by spontaneous disintegration. This retards the cooling of the earth and the estimate of its age as given above has to be completely revised.[1]

PROBLEMS

1. In the periodic flow method a rod of iron is heated at one end with a heating cycle of 4 minutes. It is found that a temperature maximum travels on the rod from one thermocouple to another at a distance of 6 cm. in 1 minute. Assuming that density of iron = 7·8 gm. per c.c., and its specific heat is 0·11 cal. per gm. per °C, calculate its thermal conductivity.

2. Steam at 100°C. is passed through a rubber tube, 14·6 cm. length of which is immersed in a copper calorimeter of thermal

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[1] For further discussion see Ingersoll and Zobel, *Mathematical Theory of Heat Conduction*, §87-90 (1913). For discussion of age of rocks from radioactive data, see Saha and Saha, *A Treatise on Modern Physics*, Vol. 1, p. 168.

capacity 23 cal. containing 440 gm. of water. The temperature of the water and calorimeter is found to rise at the rate of 0·019°C every second when they are at the room temperature (22°C). The external and the internal diameters of the tube are 1·00 cm. and 0·75 cm. respectively. Calculate the conductivity of india-rubber.

Books Recommended

1. Ingersoll and Zobel, *Mathematical Theory of Heat Conduction* (Ginn, 1913).

2. *Handbuch der Physik*, Vol. XI, pp. 42—155.

3. *Handbuch der Experimental-physik*, Vol. IX, Part I.

4. Carslaw, *Introduction to the Mathematical Theory of the Conduction of Heat in Solids* (Macmillan, 1921).

5. Carslaw and Jaeger, *Conduction of Heat in Solids* (1947), Clarendon Press, Oxford.

6. McAdams, *Heat Transmission* (McGraw-Hill, 1942).

7. Bosworth, *Heat Transfer Phenomena* (John Wiley, 1952.)

CHAPTER XV

RADIATION

15·1. Introduction.—Even when a heated body is placed in vacuum, it loses heat. In this case no heat can be lost by conduction or convection since matter, which is absolutely essential for both these processes, is absent. In such cases we say that heat is lost by 'Radiation'. To differentiate this process from conduction, it is enough to note that copper and wood, which are so much different in their conducting powers, cut off radiation equally well when placed between the hot body and the observer.

Now heat has been shown to be a form of energy, and the propagation of heat by radiation consists merely in a transference of energy. But the radiant energy in the process of transference does not make itself evident unless it falls on matter. When it falls on matter and is absorbed, it is converted to heat and can then be detected by the use of suitable methods.

Let us now study some of the properties of radiant energy. For this purpose we must have some instrument to measure it. Leslie, one of the earliest workers, used a differential air-thermometer.[1] Melloni was the first to introduce thermopiles for the measurement of radiant energy.

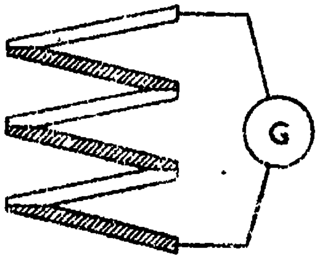

Fig. 1.—Melloni's thermopile.

In its original form, Melloni's thermopile consisted of a number of bismuth and antimony rods, placed alternately with their ends joined, as indicated in Fig. 1. The left face is blackened and forms the hot junction, while the right one is the cold junction. Radiant energy falling on the hot junction heats it and thereby produces an E. M. F. which sends a current through the circuit, and this is recorded by the galvanometer G.

The sensitiveness of these thermopiles depends not only on the couple used, but also upon the sensitiveness of the galvanometer.

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[1] The differential air-thermometer consists of a U-tube with a bulb at each end of the U. The bend contains a coloured liquid. When heat energy falls on one of the bulbs, the air contained in it expands, and forces the liquid on to the other side.

The latter must be a low resistance, voltage sensitive galvanometer. The sensitiveness also depends upon the number of thermo-junctions, but this cannot be multiplied indefinitely as the external resistance increases. The best procedure is to have the piles as light as possible and to choose a number so that the total resistance of the junctions is equal to the galvanometer resistance. For further discussion see §15·39.

As the source of radiant energy, any hot substance may be used. Leslie used a hollow metal cube or sphere filled with hot water. The surface of the cube can be coated with those substances whose emission or absorption is to be investigated.

15·2. Properties and Nature of Radiant Energy.—With the aid of these simple apparatus, it can be demonstrated that RADIANT ENERGY and LIGHT obey identical laws and have identical properties. We mention some of the points of resemblance :—

(1) Radiant Energy, like light, travels in straight lines, and forms shadows when obstructed, according to the laws of geometrical optics.

(2) It travels very quickly like light,—for the obstruction of the radiant energy coming from the sun by clouds or other means is immediately accompanied by a fall of temperature.

(3) It can travel through vacuum, for we are able to receive heat from a hot electric glow lamp though the filament which is the source of radiant energy is in vacuum.

(4) The intensity of radiant energy follows the law of inverse square, like light.

(5) Radiant energy obeys the two laws of reflection of light. This can be easily verified by placing two parabolic mirrors with their concave surfaces facing each other and their axes in the same line. If a luminous source be placed at the focus of one mirror, an image is formed at the focus of the other. If we replace the luminous source by a hot substance and put a piece of tinder at the other focus, the tinder is ignited. This shows that heat and light rays travel along the same path and hence obey the same laws.

(6) Radiant energy suffers refraction like 'light.' A spectrum may be obtained by refraction through a prism.

(7) Thermal radiation can be polarised in the same way as light by transmission through a tourmaline crystal or nicol. The polarised heat wave may be transmitted or extinguished by another nicol suitably arranged. This may be easily verified by means of a thermopile.

15·3. Identity of Radiant Energy and Light—Continuity of Electromagnetic Spectrum.—All these observations lead us to the conclusion that radiant energy is identical with light. As we shall see presently, Radiation or Radiant Energy is the general and more expressive term; light (or rather visible light) being only a kind of radiant energy which has the distinctive power of affecting the retina of the human eye, and thus producing the sensation of colour. Like other kinds of radiant energy, light is also converted into heat when it is absorbed by matter.

The identity of light and radiant energy can further be seen from the following experiments :—

(*i*) When we produce a spectrum of the sun by means of a prism, it appears to be terminated on one side by the red, and on the other side by the violet. But it can be easily seen that these limits are only apparent, and are due to the fact that the human eye is a very imperfect instrument for the detection of radiation. W. Herschel (1800) placed a blackened thermometer bulb in the invisible part beyond the red, and found that the thermometer recorded a rise in temperature. The rise in temperature was observed also when the thermometer was placed in the visible region. Thus W. Herschel discovered the *infra-red part* of the solar spectrum, and showed that it was continuous with the visible spectrum. Ritter showed that the part beyond the violet (ultraviolet) has great photographic activity.

The source of radiation in this case is the sun, which may be regarded as an intensely hot body. But it may be substituted by any sufficiently hot substance say a piece of burning coal, the positive crater of the carbon arc, or a glowing platinum wire. In these cases the intensity of radiation is not so great, and the spectrum does not extend so much towards the violet.

(*ii*) *Production of Light by Heating.*—A very simple experiment will suffice to bring out the point which has been just mentioned. Suppose we take a piece of blackened platinum wire in a dark room and pass through it an electrical current which serves to heat the wire. The magnitude of the current is gradually increased. After some time the wire becomes warm and sends out radiant energy. If a thermopile be held near it, the galvanometer connected to it shows a deflexion. When a slightly stronger current is passed the wire begins to glow with a dull red light. This shows that the wire is just emitting red radiation of sufficient intensity to affect the human eye. Accurate observations show that this takes place at about 525°C. (*Draper point*). With increasing temperature, the colour of the emitted radiation changes from *dull red* to *cherry red* (900°C.), to *orange red* (1100°C.), to *yellow* (1250°C.), until at about 1600°C. it becomes *white*. Thus the temperature of a luminous body can be estimated from its colour. Such a colour scale of temperature is given in the chart on pp. 46-47. This shows that *shorter waves are emitted by a heated body in sufficient intensity only with increasing temperature. Vice versa* we may argue that when the temperature of the wire is below the Draper point, it is emitting waves longer than the red, but these waves can be detected only by their heating effect.

Radiant Energy or Radiation is thus a more general name for Light. It can be of any wavelength form 0 to ∞ as illustrated in the chart on the following pages. Light forms less than ¾ths of an octave on the scale.

Explanation of the Chart.—We are using here the logarithmic scale, *i.e.*, log λ is plotted along the vertical line. Thus (−5) on the scale indicates that the wavelength is 10^{-5} cm., (2) indicates that $\lambda=10^{2}$ cm. As shown in the chart, visible light extends from 7×10^{-5} cm. (red) to about 4×10^{-5} cm. (violet). The infra red part was discovered by W. Herschel and the extension towards the longer wavelength side is chiefly due to the *rest-strahlen* method of Rubens and Nichols (see §15·37). These rays are detected chiefly by the thermopile, for ordinary photographic plates are not sensitive beyond the green. Beyond green, pan-chromatic plates may be used, but they are also not sensitive beyond 8,000 Å. U. Beyond this, plates dipped in dycyanine or neocyanine may be used up to 10,000 Å. U. In recent years rays as long as $\lambda=12000$ Å. U. have been photographed.

The rest-strahlen method gives us rays as long as 50μ. The longest heat ray was isolated by R. W. Wood by the method of focal isolation from a quartz mercury lamp.

ELECTROMAGNETIC WAVES

Wavelength cms	Log λ	Radiation	Generation	Detection and Analysis	Discoveror
10^{-11} Siegbahn unit	-11	Cosmic rays	Conversion of matter to Radiant Energy	Measurement of absorption coefficient	Kolhörster (1913) Millikan etc (1923)
	-10				
·06A.U.		γ-rays	Radioactive Disintegration	Photo-electric method	
	-9	X-rays Hard	Bombardment of metal targets by electrons	Crystals & Photography or Ionisation chamber.	Röntgen (1895) Laue (1912)
10^{-8} Ångström unit	-8	Medium		Fluorescence	
	-7	Soft		Reflection Grating (vacuum)	Compton (1925) Thibaud (1926)
136 A.U.	-6		Vacuum Spark	Photography	Millikan (1919) & Lyman (1906)
$1{\cdot}0\times10^{-5}$	-5	Ultra-violet		Prisms Vacuum grating	Schumann (1890) Ritter (1802)
4×10^{-5}		VISIBLE Violet	Spark. Arc Flame	Glass Quartz Fluorite	NEWTON
8×10^{-5}		Red			
μ	-4				Herschel (1840)
			Heating	Wire gratings & Thermo-couples	
	-3	Infra-red			
				Residual ray Method	Rubens & Nichols (1898)
1 mm	-2			Focal Isolation	Wood (1912)
·4 mm		Hertzian waves			Nichols & Tears (1924)
	-1	(Short)	Spark gap	Coherer	
4 mm	0				Bose (1902)

ELECTROMAGNETIC WAVES (Contd.)

Wavelength	Log λ	Radiation	Generation	Detection and Analysis	Discoveror
cms	−1				
	0		Spark gap discharge		
	+1	Hertzian waves	Triode valve Oscillator	Radar (Micro-wave Technique)	
1 metre	+2				Hertz (1887)
	3	Short-wave Broadcasting		Wireless Methods	
100 metres	4	Long-wave Broadcasting			
	5				
10^4 metres	6	Hertzian waves ↓			
	7	No upper limit			
	8				

The Hertzian waves are produced by purely electromagnetic methods (due to oscillation of current in an inductance-capacity circuit having a spark gap) and were first discovered by Hertz in 1887. Marconi applied them for wireless transmission (1894). Waves used for this purpose are generally 10—500 metres in length, though waves of about 10 km. length were used in the past. Electromagnetic waves are now almost exclusively generated by triode valves of proper design, and are used for broadcasting in three ranges :—long waves above 100 m. in length for short-range transmission, medium waves from 30 m. to about 100 m. for medium range and short waves from 30 m. to 10 m. for long-range transmission. These long electro-magnetic waves differ from the light waves only in their wavelength and attempts have been made to get shorter and shorter waves by purely electromagnetic methods so that one can pass continuously to the long infra-red rays. The limits successively reached are due to Lebedew, Lampa, Sir J. C. Bose (4 mm.), and the gap between electromagnetic waves and heat waves has been completely bridged by the work of Nichols and Tear, Arcadiewa and others.[1]

During World War II, the technique of production of waves of length from a few metres to a few centimetres has undergone a complete revolution, due to the discovery of magnetron and klystron tubes. Tubes handling powers of the order of 10^6 watts for very short period have been used for Radar (Radio Direction and Range Finding). The sensitivity of detecting methods have also increased 10^9 times. With this 10^{15} fold increase in power, the centimetre range of e.m. waves has proved an extremely potent instrument for investigation in micro-wave spectroscopy, nuclear physics, meteorology and so forth.

The ultraviolet part (rays shorter than the last visible $\lambda=3800$ Å.U.) was discovered by W. Ritter in 1802. He found that a photographic plate was affected even beyond the visible limit. Glass spectrographs usually give lines as far as $\lambda=3400$, after which either uviol glass (limit $\lambda=2800$), or quartz prisms should be used. At about $\lambda=2200$, the gelatine used in the photographic plates begins to absorb. Schumann was the first to prepare plates without gelatine and open up what is called the Schumann region. Below $\lambda=1850$ Å. U. quartz begins to absorb heavily, and Schumann therefore used fluorite spectroscopes. Beyond $\lambda=1400$, air absorbs heavily, and the whole operation of producing light and photographing the spectrum must be done in vacuum.

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[1] Nichols and Tear, *Phys. Rev.*, **21**, 587, 1923; Arcadiewa, *Zeits. f. Physik*, **24**, 153, 1924.

The pioneer in this field was Th. Lyman of Harvard, who was able to photograph lines as far as $\lambda=600$. In this region gratings have to be used for producing the spectrum.

X-rays were shown by M. von Laue in 1912 to be light waves of extremely short wavelength of the order of 10^{-8} cm., *i.e.*, about 1000 times shorter than ordinary light. He used a crystal as a diffraction grating. The shortest X-ray measured by the crystal method has the wavelength $\lambda=\cdot 05$ Å. U.

γ-rays—The term γ-rays is generally confined to e. m. rays emitted by the nuclei of atoms, and though generally they are of a shorter wavelength than X-rays, they can be sometimes of longer wave length (*e.g.*, γ-ray from Ra D). γ-rays are generally denoted by their energy content (vide p. 647), which is usually expressed in million electron volts. The wavelength of soft γ-rays can be found by X-ray methods, but for more energetic γ-rays, photoelectric methods, and Compton effect are utilised. Still more energetic γ-rays split up into a positron and an electron on passing past a nucleus (Pair-production) and their energy is calculated from the sum of the positron and electron energies.

The gap between the Lyman region (600 Å. U., and the soft X-ray region (about 20 Å. U.) has been gradually bridged by the works of Millikan and Bowen, Compton, Thibaud, Siegbahn and his pupils Eckefors, Edlen and Ericson, and others. Millikan and Bowen used ordinary vacuum spectrographs with diffraction gratings. Their source of light was condensed vacuum spark. For wavelength in this region, crystal gratings have their grating spaces too small, while the ruled gratings have their spaces too large. Compton instituted the method of obtaining spectra in this region with the aid of coarse gratings at glancing angle (see Saha and Saha, *loc. cit.* p. 273).

Since radiant heat and light are identical, all the laws and theorems of Optics and Spectroscopy can be applied to the study of radiation. But in this chapter, we shall deal with only those branches of the subject which are not studied in optics and are conventionally studied under heat. We shall first enter into a preliminary discussion regarding the passage of radiation through matter.

154. Passage of Radiant Energy through Matter.—In Optics we are accustomed to classify substances as 'transparent', 'opaque' or 'coloured.' Substances are *transparent*, if they allow visible radiation to pass through them; otherwise, they are *opaque*. If only one particular colour is allowed, we say that the substance is coloured. With respect to radiant energy, the corresponding terms are '*diathermanous*', *i.e.*, allowing the passage of radiant energy, and '*athermanous*' obstructing the passage.

Simple experiments show that substances which are usually transparent to visible radiation may be opaque to the long infrared radiation emitted from moderately heated bodies. Thus if glass is interposed between the platinum filament heated to 100°C—500°C and the thermopile, the galvanometer deflexion at once falls, showing that most of the radiation has been cut off. The best diathermanous substances are rocksalt (NaCl), sylvin (KCl), quartz, fluorite and certain other crystals.

But the terms "diathermanous" or "athermanous" lack in scientific precision. Every substance ought to be defined, so far as its transmitting or absorbing properties are concerned, with respect to a particular wavelength. We have therefore to treat the whole phenomenon from a more rigorous standpoint which is usually done in optics under the heading 'dispersion'.

Wh radiation falls on matter, it may be partly reflected, partly absorbed, and partly transmitted. We thus put

$$1 = r+a+t, \quad \ldots \ldots \quad (1)$$

where r = fraction of total energy reflected,

a = „ „ „ absorbed,

t = „ „ „ transmitted.

The value of r may be different for different wavelengths. In this case we use the subscript r_λ. Thus r_λ denotes the reflecting power of a substance for the wavelength λ, a_λ=absorption coefficient for light of wave-length λ.

From our common experience, we can define certain substances with limiting properties as regards their behaviour towards radiant energy.

(1) *Perfectly Black Bodies.*—For such bodies, $r=0$, $t=0$, $a=1$. Lampblack is the nearest approach to such a body. Apparently, it neither reflects nor transmits the light which falls on it, absorbs all, and hence appears black. But the perfectly black body is only an ideal conception, for even lampblack is found to transmit light of long wavelength. It absorbs about 96% of visible light, platinum black absorbs about 98%.

(2) *Perfectly White Bodies.*—Bodies are said to be perfectly white when $r=1$, $t=0$, $a=0$, and the surface is such that the reflection is diffuse. A piece of white chalk approximates, as far as the visible radiations are concerned, to a perfectly white body.

15·5. Theory of Exchanges (Prevost—1792).—Prior to 1792, the ideas regarding radiant energy were very much confused. People used to talk of hot radiations and cold radiations. A block of ice was supposed to emit cold radiations because it produced a sensation of cold. Prevost of Geneva was the first to recognise that this was a loose way of talking. He taught that substances at all finite temperatures emit '*radiant energy*,' but the amount increased with the temperature and is not affected by the presence of surrounding bodies. The rise or fall of temperature which is observed in a body is due to its exchange of radiant energy with surrounding bodies. This is known as *Prevost's Theory of Exchanges.*

Thus when we stand near a fire, we have the sensation of warmth because our body, *which is also a radiator*, is receiving more energy from the fire than it is losing by its own radiation. When we stand near a block of ice, we feel a sensation of cold because our body being at about 37°C loses more energy by radiation than it receives from the ice, which is at a much lower temperature, *i.e.*, 0°C. These considerations are quite general and may be applied to all similar phenomena.

15·6. Emissive Power of Heated Bodies—Preliminary Experiments.—When we have clearly recognised that every substance emits radiation by virtue of its temperature, it now becomes necessary to study how the radiation varies with temperature and properties of the body. We shall first consider the effect of the nature of the surface upon the emission and absorption of radiation. Very simple apparatus suffices for demonstrating the fundamental laws in this connection. As an emitter of radiation, we can take a Leslie cube filled with water at 100°C, and allow the radiation to fall on a concave mirror which focusses it on a thermopile. The sides of the cube may be coated with different substances to find out how the emissivity varies with the properties of these substances, provided the temperature is kept constant. It is found that at the same temperature a perfectly black surface emits the maximum energy, while a polished surface emits very little energy.

If the deflexion due to the black surface is put 100, the deflexion due to the polished surface may be as little as 8. Between these two limits may be found substances having all intermediate values. It was early recognized that radiating and absorbing powers vary together. *Good absorbers are good radiators, while poor absorbers are but poor radiators.* Substances like glass or polished metals which absorb very little, are also found to emit very little radiation.

These ideas were first grasped by Balfour Stewart but it was Kirchhoff who made them more precise. Before proceeding further it is however necessary to define the concepts used in Radiation with more rigour. We now proceed to do this in the next section.

15·7. Definitions and Fundamental Relations.

—If a body is heated, it emits radiation from its surface in all directions, which comprises waves of all lengths. The nature of the radiation depends on the physical properties of the body. Let us denote by $e_\lambda \, d\lambda$ the amount of radiation[1] of wave lengths lying between λ and $\lambda + d\lambda$, expressed in ergs and emitted per unit area of the body per second normally in unit solid angle in the direction determined by the axis of that solid angle. We may call e_λ the *emissive power* of the body. In other words

$$e_\lambda \, d\lambda = \frac{u_\lambda \, d\lambda}{dt.\, d\omega.\, dA},$$

where $u_\lambda \, d\lambda$ denotes the energy radiated normally by the elementary area dA in the elementary solid angle $d\omega$ in the element of time dt. Similarly if dQ_λ be the amount of radiant energy falling on the body in the form of radiation (λ to $\lambda + d\lambda$) and a fraction $a_\lambda dQ_\lambda$ of it is absorbed by the body and converted into heat, then a_λ is called the *absorptive power* of the body for these rays (λ to $\lambda + d\lambda$). For black bodies $a_\lambda = 1$ for all wavelengths, but for other substances a_λ depends on the physical nature of the body.

Total emission on one side.—Let us now find the total emission from a small surface element dA of a black body on one side of it. The amount of radiation emitted per second in a solid angle $d\omega$ in a direction making an angle θ with the normal to the surface is, from Lambert's cosine law,[1] equal to $dA\, e_\lambda\, d\lambda \cos\theta\, d\omega$.

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[1] The radiant intensity of a source in a particular direction, in analogy with the luminous intensity, is defined as the emergent flux from the source through a unit solid angle whose axis lies in that direction. The steradiancy of a source is defined as the radiant intensity per unit projected area of the surface, projected perpendicular to the direction of emission.

The elementary conical pencil emanating in the direction lying between θ and $\theta+d\theta$ and ϕ and $\phi+d\phi$ (see Fig. 9, p. 136) encloses the solid angle $\sin\theta\, d\theta d\phi$ and hence the emission in this direction is

$$dA\, e_\lambda\, d\lambda \cos\theta \sin\theta\, d\theta d\phi. \quad . \quad . \quad . \quad . \quad (2)$$

The total emission on the upper side of dA is therefore

$$e_\lambda\, d\lambda\, dA \int_0^{2\pi} d\phi \int_0^{\pi/2} \sin\theta \cos\theta\, d\theta = \pi\, e_\lambda\, d\lambda\, dA, \quad . \quad . \quad (3)$$

and the emission per unit area is $\pi e_\lambda\, d\lambda$.

Mutual Radiation between two small black Plates.—Let us now find the mutual radiation between two small black plates dA, dA' (Fig. 2) separated by a distance r and so oriented that the normals to the surfaces make angles θ and θ' respectively with r. The solid angle subtended by dA' at dA is $dA'(\cos\theta')/r^2$. The energy emitted per unit solid angle from dA in the direction r is $dA\, e_\lambda \cos\theta\, d\lambda$ and hence the energy emitted from dA and falling on dA' is

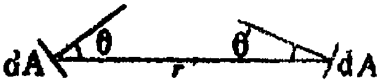

Fig. 2.—Mutual radiation between two plates.

$$\frac{e_\lambda \cos\theta \cos\theta'\, dA\, dA'\, d\lambda}{r^2}. \quad . \quad . \quad . \quad . \quad (4)$$

APPLICATION OF THERMODYNAMICS TO RADIATION

15·8. Temperature Radiation.—Since material substances at all temperatures are found to emit radiation, it becomes possible to apply the laws of thermodynamics to the problems of temperature radiation. The expression "Temperature Radiation" should be clearly understood, for matter can be made to emit radiant energy in ways other than by raising it to a high temperature, *e.g.*, by passing an electrical discharge through it when in a gaseous state, by chemical action as in flames, or by subjecting to other sources of light (phosphorescence and fluorescence). But Kirchhoff's law that $e_\lambda/a_\lambda = E_\lambda$, the emissivity of a perfectly black body, holds only for temperature radiation. For radiation produced by other methods, the law cannot be applied.

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[1] This law is experimentally found to hold for black bodies and can be deduced as a corollary of Kirchhoff's law. Non-blackbodies show large deviations from this law.

For these cases, the problem of finding out e_λ and a_λ has to be attacked by other methods. In the case of simple atoms and molecules, the problem belongs to Atomic Physics, and is successfully tackled by quantum mechanics. Sometimes the question arises whether the conditions under which luminescence is produced approximate to those of perfectly black bodies, *e.g.*, when the spectrum of an element is produced in the flame or in an electric arc; in other words, whether we can talk of the temperature of the flame or of the arc. For example an experiment is recorded by Paschen in which he measured the intensity of the D_1 and D_2 lines of sodium in a Bunsen flame, and compared it with those of the blackbody radiation within the same wavelength region. The temperature of the flame was recorded by an accurately calibrated thermocouple. He found that the D lines of sodium were twice as intense as the corresponding radiations from the black body. But this only proves that the flame cannot be regarded as a blackbody radiator and the emission of the D-lines under these conditions is due, at least partly, to causes other than temperature. The question is far too complicated to be discussed here.

15·9. Exchange of Energy between Radiation and Matter in a Hollow Enclosure (Hohlraum). Kirchhoff's Law.—Let us now take an enclosed space and let its walls be opaque to radiation of all wavelengths. The walls are first imparted a uniform temperature and then thermally insulated from the surroundings. Let us study what takes place when we place substances having widely different physical properties within this enclosure.

In the first place, the whole space is filled with radiation which is being emitted by the walls. This radiation arises out of the heat energy of the walls, and should therefore be regarded as a part of this heat energy. If we now place a small material body A inside the enclosure, it is easy to see that whatever the initial temperature of A might have been, it will ultimately acquire the same temperature as the walls.[1] This can be proved by the method of *reductio ad absurdum*, for suppose that in the equilibrium state the temperature of A is different from that of the walls. Then a Carnot engine may be used to transfer heat reversibly from the walls to A until A had the same temperature as the walls. During this process a certain amount of heat will be converted to work. But A would again be reduced automatically to a different temperature as, according to our assumption, this is the stable state of affairs. Hence the difference of temperature can be again utilized for the conversion of heat to work. We thus see that if the body were to assume a temperature different from that of the walls, we have at our disposal a means of continuously converting the heat of a single body to work without maintaining a second body at a lower temperature. This is against the second law, and hence we conclude that all material bodies placed in the enclosure would ultimately have the same temperature as the walls.

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[1] This may be easily seen for in the equilibrium state the entropy will be maximum and this can occur only when all temperature differences cease to exist.

Let us now suppose that a body of heterogeneous composition is placed within the enclosure. Then the different parts of the body have different emissive and absorptive powers. The total energy absorbed by the body will be equal to the energy it emits, since its temperature remains constant in the equilibrium state. Now the energy emitted by the body remains always the same from Prevost's law, whatever the position or the orientation of the body with respect to the enclosure. It follows therefore that the total energy absorbed by the body remains the same even if its position or orientation with respect to the enclosure is changed. And as the different surfaces of the body have different coefficients of absorption, this can be the case only when the radiation travelling inside the enclosure in different directions is identical in quantity as well as quality (*i.e.*, isotropic).

We shall now prove that the radiation inside the hollow enclosure is *independent of the nature or the geometrical shape of the walls of the enclosure* or of any body placed inside it. Suppose a body of emissive power e_λ and absorptive power a_λ is placed inside it at a large distance from the walls. The amount of energy emitted by an area dA of the body is (from eqn. 3) equal to

$$\iint e_\lambda \, d\lambda \, dA \cos\theta \, d\omega = \pi \, dA \int_0^\infty e_\lambda \, d\lambda,$$

since the limits of integration extend for all wavelengths from 0 to ∞ and throughout the whole solid angle.

For the whole body this is

$$\pi(\Sigma\, dA)\int_0^\infty e_\lambda\, d\lambda. \quad \ldots \ldots \quad (5)$$

Again the amount of energy absorbed by an element dA of the body is

$$\iint a_\lambda\, E_\lambda \cos\theta'\, d\lambda\, dA'\, \frac{dA\cos\theta}{r^2},$$

where r is the distance between an element of surface dA' of the enclosure and dA of the body, E_λ the emissive power of the enclosure and θ' the angle made by the normal to dA' with the direction of emission. The above expression is equal to

$$\iint a_\lambda\, E_\lambda\, d\lambda.\, dA\cos\theta.\frac{dA'\cos\theta'}{r^2} = \iint a_\lambda\, E_\lambda\, d\lambda\, dA\cos\theta\, d\omega$$

$$= \pi\, dA\int_0^\infty a_\lambda\, E_\lambda\, d\lambda,$$

and for the whole body, the absorption is

$$\pi(\Sigma\, dA)\int_0^\infty a_\lambda E_\lambda\, d\lambda. \quad \ldots \ldots \quad (6)$$

Hence equating (5) and (6) we get

$$\int_0^\infty e_\lambda\, d\lambda = \int_0^\infty a_\lambda\, E_\lambda\, d\lambda. \quad \ldots \ldots \quad (7)$$

Now this equality must hold for each portion of the spectrum, because if for any part of the spectrum it did not hold, *i.e.*, the absorbed part be not equal to the emitted part, there will be a continuous increase or decrease of radiant energy of that particular wavelength at the expense of energy of other wavelengths, and hence E_λ would increase or decrease with time. This is contrary to our definition of E_λ. Hence for each wavelength

$$e_\lambda = a_\lambda\, E_\lambda \quad \ldots \ldots \quad (8)$$

Now if we place the same body in another enclosure maintained at the same temperature but having different shape and nature of walls, we shall have

$$e_\lambda = a_\lambda\, E_\lambda'.$$

since e_λ, a_λ depend upon the nature of the body and its temperature and not upon the surroundings. Hence

$$E_\lambda = E_\lambda'.$$

From equation (8) we easily see that if we place a black body ($a_\lambda = 1$) inside the enclosure, E_λ is equal to the emissive power of this black body. Thus we see that the radiation inside a hollow vessel is independent of the nature and shape of the walls and is identical in every respect with the radiation emitted by a black body at the same temperature as the enclosure.

We can now readily deduce the relation between emissive power and absorptive power (Kirchhoff's law). From equation (8) we have

$$\frac{e_\lambda}{a_\lambda} = E_\lambda$$

i.e., at any temperature the ratio of the emissive power to the absorptive power of a substance is constant and equal to the emissive power of a perfectly black body. This is Kirchhoff's law and has been proved here from thermodynamical considerations. We have proved the law here for bodies inside the enclosure. A little consideration will show that, since the emissive and absorptive powers depend only upon the physical nature of the body and not upon its surroundings, the law will hold for all bodies under all conditions for pure temperature radiation.

A simpler but less rigorous proof of Kirchhoff's law is obtained by omitting the geometrical considerations mentioned above. Imagine the enclosure to be filled with radiation having wavelength lying between λ and $\lambda + d\lambda$, and let a body be placed inside it. Then equating the energy emitted by the body to the energy absorbed, we have

$$e_\lambda \, d\lambda = a_\lambda \, dQ,$$

where dQ is the energy of the incident radiation. Or

$$\frac{e_\lambda}{a_\lambda} = \frac{dQ}{d\lambda}.$$

In the case of a perfectly black body of emissivity E_λ we have (since $a_\lambda = 1$),

$$E_\lambda \, d\lambda = 1 . dQ.$$

$$\therefore \quad \frac{dQ}{d\lambda} = E_\lambda.$$

Hence

$$\frac{e_\lambda}{a_\lambda} = E_\lambda.$$

15·10. The Black Body.—The considerations put forward in the last section enable us to design a perfectly black body for experimental purposes. We have seen that if an enclosure be maintained at a constant temperature it becomes filled with radiation characteristic of a perfectly black body. If we now make a small hole in the wall and examine the radiation[1] coming out of it, this diffuse radiation emerging out of the hole will be nearly identical with radiation from a perfectly black emissive surface. The smaller the hole, the more completely black the emitted radiation is. Thus a correction[2] has to be applied for the lack of blackness due to the finite size of the hole. This is due to the fact that some of the radiation coming from the enclosure is able to escape out and the state of thermodynamic equilibrium as postulated in the last section does not hold. Further the escaping radiation should consist of as little direct emission and reflection from the wall as possible. This is almost completely avoided in the particular type of black body due to Fery (Fig. 4). So we see that the uniformly heated enclosure with a small cavity behaves as a black body towards emission.

Again such an enclosure behaves as a perfectly black body[3] towards incident radiation also. For any ray passing into the hole will be reflected internally within the enclosure and will be unable to escape outside. This may be further improved by blackening the inside. Hence the enclosure is a perfect absorber and behaves as a perfectly black body.

Though Kirchhoff had proved in 1858 that the radiation inside a uniformly heated enclosure is perfectly black, it was long afterwards in 1895 that Wien and Lummer utilised this conception to obtain a black body for experimental purposes.

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[1] This radiation is made up of single, double, treble etc. reflection from the walls. Thus if the reflecting power of the surface of the wall is r while the emission from the surface is e, the total radiation escaping out is $e+er+er^2+\ldots\ldots=\frac{e}{1-r}$. From Kirchhoff's law $e=Ea=E(1-r)$ from (1) if the walls are assumed to be opaque and impervious to radiation ($t=0$), E being the emission from a black body. Hence the total radiation escaping out is simply equal to E, the emission from a black body.

[2] See Wien and Lummer, *Wied. Ann.*, **56**, 451, 1895; Buckley, *Phil. Mag.*, **6**, 447, 1928.

[3] Kirchhoff defines a black body as one "which has the property of allowing all incident rays to enter without reflection and not allowing them to leave again." See Planck, *Wärmestrahlung.*

The black body of Wien consists of a hollow cylindrical metallic chamber C (Fig. 3) blackened[1] inside and made of brass or platinum, depending upon the temperature that it has to stand. The cylinder is heated by an electric current passing through thin platinum foil as indicated by thick dashes. The radiation then passes through a number of limiting diaphragms and emerges out of the hole O. The cylinder is surrounded by concentric porcelain tubes. The temperature of the black body is given by the thermoelement T. This is the type of black body now commonly used.

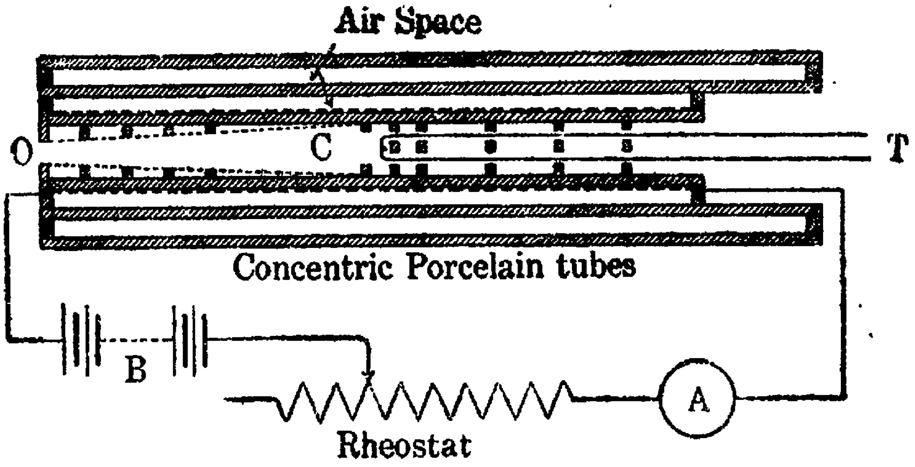

Fig. 3.—The black body of Wien.

Another type due to Fery is shown in Fig. 4. Note the conical projection P opposite the hole O. This is to avoid direct radiation from the surface opposite the hole which would otherwise make the body not perfectly black.

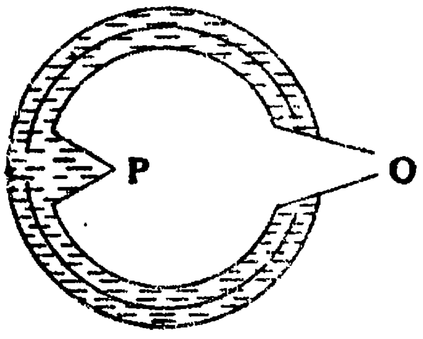

Fig. 4.—Black body due to Fery.

A striking property of such an enclosure is that if we place any substance inside it, the radiation emitted from it is also black and independent of the nature of the body. Thus all bodies inside the enclosure lose their distinctive properties. For a mirror placed inside will reflect the black radiation from the wall and hence the emitted radiation is black. Any substance, if it absorbs any radiation transmitted from behind, must emit the same radiation in consequence of Kirchhoff's law, and the total radiation leaving it must become identical with that from the walls, *i.e.*, of a black body.

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[1] The walls, however, need not be black. Blackening merely enables the equilibrium state to be reached quickly.

15·11. Applications of Kirchhoff's Law.—The law embodies two distinct relations, a qualitative and a quantitative one. Qualitatively, it implies that if a body is capable of emitting certain radiations it will absorb them when they fall on it. Quantitatively, it signifies that the ratio is the same for all bodies.

Various experimental proofs and observations may be cited in support of the qualitative relation. If a piece of decorated china is heated in a furnace to about 1000°C. and then taken out suddenly in a dark room, the decorations appear much brighter than the white china, because they being better absorbers, emit also much greater light. If we take a polished metal ball and have a black spot on it by coating it with platinum black, then on heating the ball to about 1000°C and suddenly taking it out in a dark room, it will be found that the black spot is shining much more brilliantly than the polished surface. Again take the case of a coloured glass. We know that green glass looks green because it absorbs red light strongly and reflects or transmits the green (red and green being complementary colours). Hence when a piece of green glass is heated in a furnace and then taken out, it is found to glow with a red light. Similarly a piece of red glass is found to glow with a green light. A more decisive example illustrating selective action is that of erbium oxide, didymium oxide, etc., which when heated emit certain bright bands in addition to the continuous spectrum. If now a solution of these oxides is made and continuous light is passed through it, the very same bands appear in absorption.

15·12. Application to Astrophysics.—Besides these applications Kirchhoff's law was in a sense responsible for the birth of two entirely new branches of Science, *viz.*, Astrophysics (Physics of the Sun and the Stars) and Spectroscopy. We shall recount here briefly how these develpoments grew out of Kirchhoff's law. Newton had shown in 1680 that sunlight can be decomposed by means of a prism into the seven colours of the rainbow, (see Fig. 5(*a*)), but Fraunhofer, who repeated the experiment in 1801 with better instruments, found to his surprise that the spectrum was not continuous, but crossed by dark lines (Fig. 5 (*b*)). Their number is at present known to be about 20000, but Fraunhofer noticed about 500 of them, and denoted the more prominent bands by the letters of the alphabet :—A, B, C.... For a complete list see Revision of Rowland's Preliminary Table of Solar Wave lengths issued by the Mount Wilson Observatory.

Fraunhofer never understood how these dark lines originated, neither did any of his contemporaries. But he realized their great importance, measured them and catalogued their wavelengths. He examined the light from stars and showed that their spectra were also crossed by dark lines just as in the case of the sun. A typical stellar spectrum is shown in Fig. 5 (*e*).

In the meantime, however, other sources of light were examined by the spectroscope and some knowledge was obtained of their spectra. It was found that a glowing solid gives a continuous spectrum, but a flame tinged with NaCl gives a pair of intense yellow lines on a dark background. It was found that if an electric discharge was passed through a glass tube containing gas at low pressure, a large number of emission lines was obtained on a dark background. For hydrogen these are shown in Fig. 5 (*d*).

But still the dark lines of Fraunhofer remained unexplained. Some physicists, notably Fizeau, observed that if the spectrum of the sun is examined side by side with the spectrum from a sodium flame, the yellow lines appear in the same place as the D-band of the Fraunhofer spectrum. Similar is the case with the hydrogen spectrum. In Fig. 5 (*c*) and (*d*) we see the emission spectrum of hydrogen side by side with the Fraunhofer spectrum. It is clearly seen that some of the dark lines in the latter occur in the same place as the bright lines in the former.

The explanation given by Kirchhoff not only completely solved the problem but was far-reaching and extremely fruitful in its consequences. He supposed that the central body of the sun consists of a glowing mass which emits a continuous spectrum without black lines. But this light has to pass through a cooler atmosphere surrounding the central mass. In this atmosphere, which is at a very high temperature, all the elements like Na, Cu, etc., exist in the gaseous form.

We have seen how the early workers studied the phenomenon of radiation with simple apparatus and had arrived at some very general laws. Every substance when heated emits radiation, *i.e.*, light. Every substance has again got the power of absorbing light. Kirchhoff arrived at the same law from thermodynamic reasoning (§15·9) and applied it to explain the dark lines as follows :— Sodium can emit the D-lines when it is excited; hence when light falls on it, it can absorb also the same light, and allows other light to pass through it unmolested. The gases in the outer cooler mantle round the sun therefore deprive

PLATE II

Continuous Prismatic Spectrum

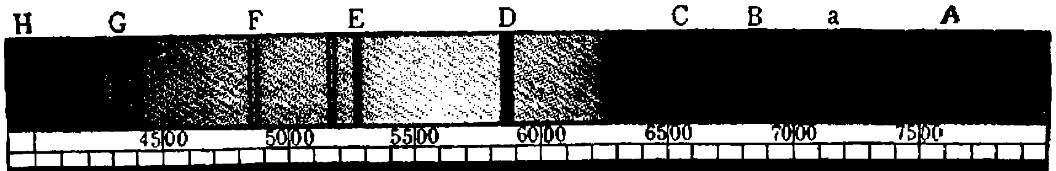
(a)

Continuous Grating Spectrum

(b)

Solar Absorption Spectrum (Grating)

(c)

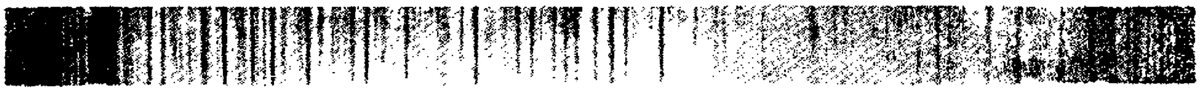


(d)

Emission Spectrum of hydrogen showing Balmer lines

Spectrum of α-Auriga (G_0 type)

(e)



Comparison of the flash spectrum (1905) with Rowland Atlas (Flash photograph enlarged six times and Atlas reduced to five times). The spectrum was photographed by S. A. Mitchell.

(f)

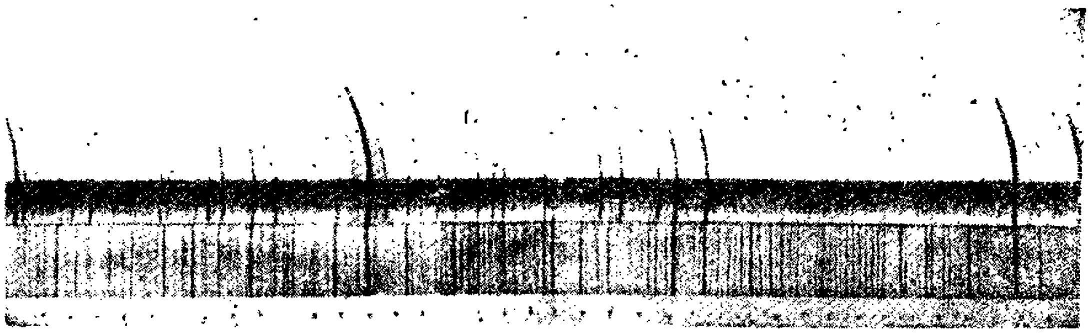


Fig. 6

Figs. (a), (b), (c), (d) have been reproduced from Knowlton, *Physics for College Students*, (e) from Müller-Pouillets, *Lehrbuch der Physik*, Vol. IV and (f) from *Handbuch der Astrophysik*, Vol. IV.

the continuous spectrum from the central mass, of the lines they themselves can emit, and give rise to the black lines. The D-bands (absorption spectrum of sodium) in the Fraunhofer spectrum therefore prove that there is sodium in the sun's atmosphere. Similarly the other dark lines testify to the presence of their respective elements in the atmosphere of the sun.

The correctness of Kirchhoff's explanation is seen further from flash spectrum results. We have supposed that the atmosphere of the sun contains Na. Now if we could observe the spectrum of the atmosphere apart from that of the central glowing core (the photosphere), the lines would appear bright. We cannot ordinarily do it because the solar atmosphere is so thin that we cannot cover up the disc properly, leaving the atmosphere bare; the scattered sky-light which is due to the scattering of the sunlight by the molecules and dust particles in the atmosphere completely obscures the spectrum outside of the disc. But during a total solar eclipse, the solar disc is completely covered, and the sky-light is also reduced by the moon's shadow. To any one observing the sun through a spectroscope, the solar atmosphere will be laid bare at the time of totality and the dark lines will flash out as bright lines. This was found actually to be the case by Prof. Young in 1872. Fig. 5 (*f*) shows a flash spectrum of 1905 eclipse which is placed side by side with Rowland Atlas for the sake of comparison. The lines of the flash spectrum are thus found to be due to the elements in the sun's atmosphere.

But Kirchhoff's discovery is of much more far-reaching importance than the mere success in explaining the Fraunhofer bands would indicate. It clearly asserted for the first time, *that every different type of atom, when it is properly excited, emits light of definite wavelength which is characteristic of the atom.* Just as a man is known by his voice, or a musical instrument by the quality of its note, so each atom can be recognised by the particular lines it emits. Thus was born the subject of Spectrum Analysis, which aims at identifying elements by their characteristic lines, and forty new elements were added with its aid to the list already known. The different atoms are regarded as so many different types of instruments, each capable of producing its own characteristic etherial music.

15·13. Quantitative Proof of Kirchhoff's Law—Pflüger's Experiment.

—A quantitative proof of Kirchhoff's law has been provided by the experiments of Pflüger.[1] He measured the emission and absorption due to a thin tourmaline crystal for both the ordinary and the extraordinary rays. His apparatus is diagrammatically illustrated in Fig. 6.

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[1] *Ann. d. Physik*, 7, 806, 1902.

S_1 is a source of light, radiation from which is concentrated by means of the lens L_1 on a very thin tourmaline plate T (the plate is so thin that it may not absorb the ordinary ray). The light is again concentrated by the lens L_2 to fall on the slit of the collimator C_1, and then falls on a Lummer-Brodhun spectrophotometer. This consists of a cube W, prism P and telescope F. The cube is prepared by cutting any cube diagonally and silvering the diagonal surface. The intensities of light reflected and transmitted by the silver film are equal. S_2 is a standard source of light for comparison and C_2 a collimator. Light coming from S_2 and reflected from the film, as well as direct light from S_1 enters the nicol N.

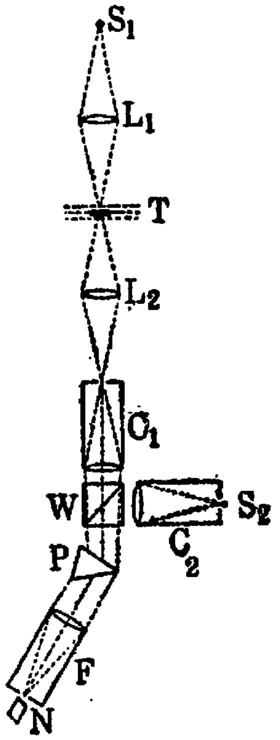

Fig. 6.—Pflüger's experiment.

The tourmaline plate T is first maintained at any desired temperature and the emission from it, when S_1 is removed, is compared with the light from S_2 for any particular wavelength as given by the prism P. The nicol N enables the comparison to be made for both the ordinary and the extraordinary rays. Next S_1 is placed in position and comparison effected. Lastly T is removed and the light from S_1 directly compared. To facilitate this a rotating sector was placed in front of S_1 to transmit only a part of the light.

The calculations can be easily made. Let I denote the intensity of the incident beam, then a fraction r of it is reflected at the first face of the crystal r is equal to $\left(\frac{\mu-1}{\mu+1}\right)^2$ where μ is the refractive index of the crystal for the particular ray. The remaining fraction $(1-r)$ is available for transmission. Let the fraction of light reaching the other face be $1-r-a$, a being the absorption coefficient. The fraction transmitted through the crystal is $1-r-a=t$. The amount transmitted $= It = I(1-r-a)$. Now the observations give E_o, E_e the emission from the crystal corresponding to the ordinary and extraordinary rays, I_o, I_e, the intensities of the light emitted from the source S_1; and $E_o+I_o t_o$, $E_e+I_e t_e$ when both S_1 and T emit light. From these t_o and t_e can be determined and hence also a_o, a_e since r_o, r_e can be calculated from a knowledge of μ_o and μ_e.

Pflüger found that $a_e/a_o=0\cdot650$ and $E_e/E_o= 0\cdot641$. These are very nearly equal, hence $E_e/a_e=E_o/a_o$, or the ratio of the emissive and absorptive powers is the same for both the ordinary and the extraordinary rays. This proves Kirchhoff's law quantitatively for each polarised component.

The ratio $E/a=$ constant holds for temperature radiation only. For coloured substances possessing a selective absorption without corresponding emission $E/a = 0$, and for luminous gases showing no absorption $E/a=\infty$. But in these cases Kirchhoff's law cannot be applied since there is no true temperature radiation.

OTHER PROPERTIES OF RADIATION

PRESSURE OF RADIATION

15·14. General Ideas.—As radiation has been shown to be identical with light, it possesses all the properties which are ascribed to light. One of the properties of light most important for our present purpose is that it exerts a small but finite pressure on surfaces on which it is incident. Though this property was in fact suspected by philosophers for a long time since the days of Kepler, who arrived at the conclusion from the observation that, as the comets

Fig. 7.—Tail of the comet.

approach the sun, the tail of the comet continuously veers round so as to be always opposite the sun (Fig. 7, p. 639). This he tried to explain on the assumption that solar light exerts pressure on all material bodies exposed to it, but the pressure increases in importance only when the size of the particle is reduced. As painstaking experimental investigations failed to show the existence of light pressure, the view was abandoned for a long time, but Maxwell propounded in 1870 his Electromagnetic Theory of Light, and showed that light should exert a pressure, but this is very small, being equal to the energy density of light for a parallel beam. For a proof of this theorem from the electromagnetic theory of light see Planck, *Wärmestrahlung*, Part II, Chap. I. Thus we see that in order to find the pressure due to incident radiation we first find out an expression for the energy density of radiation.

It can be easily shown that in the case of a *parallel* beam the energy density ρ of radiation is equal to I/c where I is the intensity of radiation and c the velocity of light. For, by definition, I is the amount of radiant energy incident per second on a unit area held perpendicular to the incident beam. This radiation will travel in a second a distance c and will consequently fill a cylinder (Fig. 8) of unit base area and of height c, and hence of volume c. The density of radiation ρ is simply the amount of radiation contained in unit volume, and is therefore equal to I/c. Now by the above theorem.

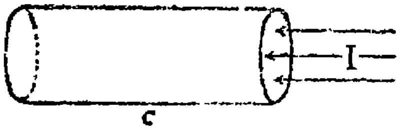

Fig. 8.—Energy density in a parallel beam.

$$p=\rho=\frac{I}{c}\,. \qquad \qquad (9)$$

We may now give some idea of the magnitude of the pressure exerted by sunlight. The solar constant, *i.e.*, amount of heat received by 1 cm.^{2} of a black surface exposed to solar rays is found to be 1·94 calories per minute. Hence

$$I=1{\cdot}94\times4{\cdot}2\times10^7/60 \text{ ergs per sec. per cm.}^2$$

$$\therefore\quad p=I/c=4{\cdot}5\times10^{-5} \text{ dynes/cm.}^2$$

Thus the pressure exerted by sunlight on 1 sq. cm. is equal to the weight of $4{\cdot}6\times10^{-8}$ grams of matter.

15·15. Energy Density and Pressure of Diffuse Radiation.—In the case of diffuse radiation however the relation is not so simple. Let us find the density of radiation inside a uniformly heated enclosure of any shape. Take a very small element of volume v inside the vessel at a large distance from the walls. All the radiation inside v may be assumed to come from a sphere described about any point O inside v, the radius r being very large compared with the dimensions of v. Let the radiation coming from a surface element dA of the vessel traverse along the radius (Fig. 9) and intersect v in a length l. Describe an elementary cone with a point in dA as the vertex and the radial line as the axis. The solid angle of such an elementary cone is f/r^2 where f is the area of the cross-section perpendicular to the radius. The radiation will take a time $t=l/c$ in traversing the volume v and hence the amount of radiation contained in v due to this elementary cone is, from (4) equal to, since θ is always nearly zero,

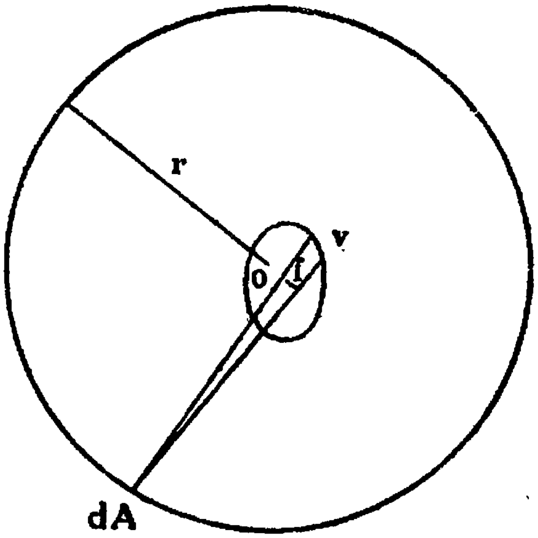

Fig. 9.—Energy density of the diffuse radiation.

$$K\,dA\,\frac{f}{r^2}t = K\frac{dA}{r^2}\cdot\frac{fl}{c},$$

where K is the specific intensity of radiation, *i.e.*, the amount of radiation proceeding in a particular direction per unit solid angle across unit area per unit time.

The total amount of radiation coming from dA and contained in v is found by summing over all the elementary cones, and is therefore equal to

$$\frac{K}{c}\frac{dA}{r^2}\sum fl = \frac{K}{c}\frac{dA}{r^2}v.$$

The total energy contained in v due to the entire enclosure will be found by summing the above expression over all elements dA of the sphere. Hence it is equal to

$$\frac{Kv}{c}\sum\frac{dA}{r^2} = \frac{Kv}{c}4\pi,$$

since dA/r^2 represents the solid angle subtended by the element dA at the point O. Hence the energy density of radiation inside the enclosure is given by

$$u = \frac{4\pi K}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

It can now be easily shown that the pressure due to this diffuse radiation is $u/3$. Consider a surface AB (Fig. 10) on which radiation is incident in a direction making an angle θ with the normal. The density of radiation in the enclosure due to radiation coming from the direction enclosed in a very small solid angle is $K\,d\omega$. This may be treated as linear. Hence the pressure on AC due to the radiation coming from the direction θ, ϕ is $K\,d\omega/c$ where $d\omega = \sin\theta\,d\theta\,d\phi$. The total force exerted on AC, is $(K\,d\omega/c)$. AC, which is also the total force on AB. Its normal component is $(K d\omega/c) \times$ AC $\cos\theta$. Hence the pressure on AB normally per unit area due to radiation incident on it in the direction θ, ϕ is

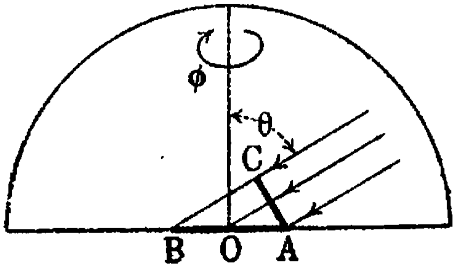

Fig. 10.—Diffuse radiation incident on the surface AB.

$$\frac{K}{c}\,d\omega.\,\frac{\text{AC}\cos\theta}{\text{AB}} = \frac{K}{c}\cos^2\theta\,d\omega.$$

Integrating over the entire hemisphere we get the total pressure

$$p = \int_0^{\pi/2}\!\!\int_0^{2\pi} \frac{K}{c}\cos^2\theta\sin\theta\,d\theta\,d\phi = \tfrac{1}{3}.\,2\pi\,\frac{K}{c}.$$

The energy density u in the space is given by $u = 2\pi K/c$. Hence

$$p = \frac{u}{3}. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

15·16. Bartoli's Proof of the Existence of Pressure of Radiation.—We shall now give the thermodynamical proof of the existence of radiation pressure due to Bartoli. He conceived an imaginary process in which he takes a cylinder with perfectly reflecting surfaces, and closed by two perfectly conducting black plates C, D (Fig. 11). These plates are placed in contact with two heat-reservoirs of infinite capacity kept at temperatures T, T', so that their temperatures are maintained constantly at T and T' ($T' > T$). A and B are two perfectly reflecting diaphragms, and B is provided with a valve. Suppose that, to

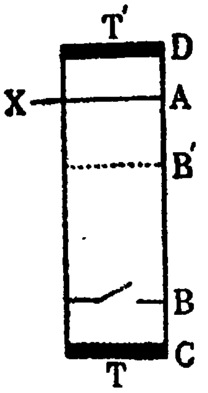

Fig. 11.—Bartoli's cylinder with diaphragms etc.

start with, the valve in B is open, and A is in the position shown, so that the space AB is filled up with radiation in equilibrium with a black body at temperature T, the small space AD is filled with radiation which is in equilibrium with a black body at temperature T'. Then we close the valve, and move B upwards thereby compressing the radiation imprisoned in the space AB to a very small volume so that the density of radiation in space AB′ (B′ is the final position of B) is much larger than in AD. If now A is pulled aside, the space in B′D will contain much more radiation than can remain in equilibrium with the black body T'. This excess energy will therefore be absorbed by T' till equilibrium is reached. In this process, the net result is that we have transferred heat from a colder body to a hotter body, but from the second law this will be rendered possible only by the expenditure of work. So we must have done some work in moving B upwards. Hence we conclude that as B moves upwards, it must be opposed by a pressure, and this can be due only to radiation.

15·17. Analogy between Black Radiation and a Perfect Gas.—The ideal process described above brings out clearly the close analogy between black radiation and perfect gas which proved rather far-reaching in its consequences, and resulted in the discovery of the laws of temperature radiation. In the Kinetic Theory, we picture a perfect gas as being an assembly of particles in perfect chaos, *i.e.*, having all velocities from 0 to ∞, and moving in all directions. We observe that black radiation, *i.e.*, radiation in an enclosure, is also proceeding in all directions, and is composed of waves of all lengths. In the case of a perfect monatomic gas, the pressure exerted is 2/3rd the energy density; the factor 3 in the denominator being due to the fact that only the component of motion perpendicular to the wall is effective in producing the pressure. In the case of light also, the light waves carry momenta and exert pressure when they are incident on the walls. When these are perfectly absorbing no wave is reflected, and pressure of radiant energy is equal to 1/3 density of radiation. If the walls are perfectly reflecting, the pressure is again equal to 1/3 the total energy density of radiation.[1]

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[1] The difference in the two cases viz. 2/3 for molecules and 1/3 for photons (radiation) is simply due to the high velocity of photons and is easily explained from relativistic mechanics, the two phenomena being exactly similar.

The analogy can be further worked out. We can regard the black radiation as a thermodynamic system and calculate its energy as well as entropy. Later developments allowed the analogy to be pushed still further. Radiant energy is now regarded as atomic in structure, consisting of discrete particles called *photons* which retain their total stock of energy unimpaired throughout their flight in space, and may only be broken up on their encounter with matter.

In a blackbody chamber the photons may have all energies between 0 and ∞, and may be moving in all possible directions. Just as in the kinetic theory of gases we have to find out how many molecules at a given temperature have a definite range of energy (Maxwell's law of distribution, p. 132), so also in the theories of radiation we have to find out how many quanta of frequency ν are contained in a black radiation chamber. This is treated in Chap. XVII.

15.18. The Quantum Theory of Light.—This concept of light, which appears to be diametrically opposed to the view that light is a wave motion, is nevertheless forced upon us by a number of facts which came to light about the beginning of the present century. It will suffice to take only one phenomenon, *viz.*, *Photoelectricity*.[1] It was found that when ultraviolet light fell on an insulated metallic plate, the latter became positively charged. This is due to the fact that light, when it falls on a metallic plate and gets absorbed, releases electrons which escape into the surrounding space and leave the plate positively charged. The velocity of these electrons is measured as usual by the method of crossed electric and magnetic fields, and is found to vary from a maximum value to zero.

In course of further investigation on the subject, certain surprising facts came to light. It was found that photoelectrons were emitted only when the plate was illuminated by light *rich in ultraviolet rays*, but no photoelectron was emitted when the plate was illuminated by *red light*, however intense this might be. Lenard pursued the subject further; he illuminated the plate with light of one colour (monochromatic) and measured the maximum velocity with which the electrons are emitted. This was done for five or six different rays. Einstein showed in 1905 from Lenard's experimental results that if the energy E with which the electron is emitted is plotted against the frequency of the illuminating light a straight line is obtained. We have

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[1] The photoelectric phenomenon was actually discovered by Hertz, but the gradual clearing up of the ideas is due to Hallwachs, Righi, and Lenard. For further information, see *A Treatise on Modern Physics* by Saha and Saha, pp. 186—188.

$$E = \alpha(\nu-\nu_0), \quad . \quad . \quad . \quad . \quad (12)$$

where α is a constant.

This shows that if the plate be illuminated with light of frequency less than ν_0, no electron can be emitted. ν_0 is known as the *photoelectric threshold frequency.*

It is easily seen that this equation is contradictory to the usual conceptions of light propagation or absorption. According to the classical conception, light as it is propagated in space from a central source goes on thinning itself in the manner given by the inverse square law. Thus if we have a source emitting Q units of energy per unit time, then the amount flowing through unit surface at distance r is given by $Q/4\pi r^2$, and if r be large enough, $Q/4\pi r^2$ may be as small as we please.

Now to return to the case of release of electrons from metallic surfaces. The electron may be supposed to be held to the parent atom by a certain force of attraction, and when it receives a certain minimum amount of energy from outside, it will leave the atom. It can receive this energy from light only by absorption. The energy absorbed by an atom in the metal is

$$\frac{Q}{4\pi r^2}\, a.A.t, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where A=area of the atom exposed to light, t=the time for which light is incident and a is the absorption coefficient.

But a little consideration shows that in photoelectric emission light cannot be absorbed according to this process. For if this were the case, we can obtain photoelectrons by illuminating a metal plate with red light for a sufficiently long time. This is never found to be the case; red light, however strong, never releases a single photoelectron, however long the metal plate may remain exposed to it. On the other hand, violet light, however feeble it may be, releases the electrons instantaneously.

N. R. Campbell has cited a specific case which illustrates this point clearly. In a certain experiment the intensity of the spark light was so much diminished that, according to equation (13), 45 minutes are required before an atom can absorb sufficient light for the ejection of an electron. In this case, A was taken$=10^{-16}$ sq. cm. But the ejection was found to be instantaneous.

These facts can be explained only by abandoning the ideas sketched above as regards propagation, and assuming that light is atomic in structure. Each atom of light retains its total energy-content intact as it flies through space.

With this conception Einstein explains the photoelectric phenomenon in the following way. Let us suppose that the amount of energy contained in a cell of light is proportional to ν, and may be put equal to $h\nu$. When the cell of light (or Photon) falls on the atom and is absorbed by it, a part of the energy is spent in releasing the electron from the parent system, the remaining part is converted to the energy of the photoelectron according to the law of conservation of energy. We have

$$\underset{\text{(Energy of ejection)}}{E} \quad + \quad \underset{\text{(energy of Release)}}{A} \quad = h\nu,$$

$$E = h(\nu - \nu_0). \qquad . \quad . \quad . \quad . \quad . \quad (14)$$

The constant 'h' is generally known as *Planck's universal constant*, because Planck was the first to arrive at the quantum theory of light from his investigations on black body radiation. Its value is $6{\cdot}54 \times 10^{-27}$ ergs × sec. Equation (14), generally known as Einstein's Photoelectric equation, has been extensively verified by the experiments of Millikan.[1]

The theory of light-quanta indeed effected a revolution in our conception of Physics. We have therefore introduced it at an earlier stage than is usually done. It may, however, be remarked that the quantum theory does not supersede the wave theory entirely, but rather supplements it. A synthesis of the two views has been affected by de Broglie, Heissenberg and Schrödinger in what is now called "Wave Mechanics".

Planck's law that the energy-content of a radiation-quanta $\epsilon = h\nu$, enables us to characterise radiation by its energy-content. We have

$$\epsilon = h\nu = hc/\lambda$$

so that the energy-content of a wave of length λ Å units is given by

$$\epsilon = \frac{6{\cdot}54 \times 10^{-27} \times 3 \times 10^{-10}}{10^{-8}\,\lambda} \text{ ergs} = \frac{1{\cdot}96 \times 10^{-8}}{\lambda} \text{ ergs.} \qquad (15)$$

It is the usual practice to express ϵ in another unit, viz. the electron-volt. This is the energy acquired by an electron in falling through 1 volt and is therefore equal to $\dfrac{4{\cdot}80 \times 10^{-10}}{300} = 1{\cdot}60 \times 10^{-12}$

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[1] *Phys. Rev.*, **7**, pp. 18, 355, 1916.

ergs. We see easily that a radiation quantum having the wavelength λ Å. U. will have the energy of y electron volts, where

$$y = \frac{hc \times 300}{\lambda \times 4{\cdot}80 \times 10^{-10} \times 10^{-8}} = \frac{12340}{\lambda} . \quad . \quad . \quad (16)$$

Thus the D_1-light from Na has the energy of $\frac{12340}{5896} = 2{\cdot}2$ e.v., the Kα-line of Cu ($\lambda = 1{\cdot}53$ Å.U.) has the energy $\frac{12340}{1{\cdot}53} = 8000$ e.v., a γ-ray $1{\cdot}23 \times 10^{-11}$ cm. in wavelength the energy of 1 million electron-volts. γ-rays having an energy of 2·66 m.e.v. are emitted by ThC$''$, and in nuclear reactions, γ-rays having the enormous energy of 17 m.e.v. have been found.

15·19. Pressure of Light from the Quantum Theory.—The pressure of light can be deduced from the Quantum Theory also. Let us consider a photon $h\nu$ moving with the velocity c. According to the Theory of Relativity, *mass and energy are identical, being connected by the relation*[1] $E = mc^2$. Hence a photon of energy-content $h\nu$, moving with the velocity c, may be supposed to possess a mass $m = h\nu/c^2$. The photon therefore carries the momentum $mc = h\nu/c$. If it is incident normally on a black surface and is absorbed by it, it exerts an impulse$= h\nu/c$. The totalpressure exerted$= \Sigma\, h\nu/c$, where the summation extends over photons of all frequencies incident on the plate per unit time. $\Sigma\, h\nu$ is clearly equal to I, the intensity of light. Hence we have the theorem $p_r = I/c$ where I is the intensity of incident light.

For *diffuse* radiation it is easy to see, as in the corresponding case for gases, that

$$p_r = \frac{1}{3} \cdot \frac{I}{c} .$$

15·20. Experimental Proof of the Existence of Radiation Pressure.—The pressure of radiation is so small (*vide* p. 641) that for a long time it baffled all attempts to measure it. The difficulties were overcome only in 1900 when Lebedew,[2] and a little later Nichols and Hull,[3] successfully demonstrated its existence. The straightforward way is to mount a pair of vanes A composed of absorbing or reflecting surfaces, on the arms of a glass cross, and suspend it by means of a thin quartz fibre f within a bell-jar (Fig. 12). A mirror m is attached to the suspension and the deflection is measured by the lamp and scale arrangement as for galvanometers. Light from a strong source is focussed on one of the vanes, and the resulting deflection is measured. If the constants of the suspension are known, the pressure can be easily calculated from the deflection, and compared with the theoretical value I/c. The value of I is determined calorimetrically by substituting a black copper block of special design at the position occupied by the vane and allowing the light to fall on it. The block is so designed that it absorbs all the light which falls on it. The rise in temperature of the block is noted, from which I can be easily determined.

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[1] This theorem is due to Einstein. A. H. Compton has given an experimental demonstration of the momentum carried by photons (Compton-effect). See *Phys. Rev.*, **21**, 483, 1923.

[2] *Ann. d. Physik*, **6** 438, 1901.

[3] *Jour. Amer. Acad.*, April; 1903; *Phys. Rev.*, **13**, 293, 1901; Hull, *Phys. Rev.* May, 1905.

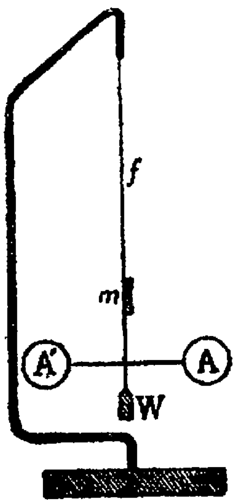

Fig. 12.—Apparatus for measuring pressure of light.

In such experiments the disturbing factors have been found to be due to three distinct causes:—

(1) The *Radiometer action*, which causes a rotation of the vane due to the unequal heating of its two sides. This is proportional to the pressure of the surrounding gas and to the temperature difference, and is in general much greater than the true radiation pressure.

(2) *Convection Currents*, due to the rush of air towards the parts warmed by the passage of the pencil of rays.

(3) *Rocket action*, due to the escape of particles of gas from the surface of the vanes when these are heated by the incident light. On account of this the vane experiences a recoil.

It is seen that the factors mentioned in (1) and (2) are eliminated by suspending the vanes in the highest vacuum and taking as thin a strip for the vanes as possible. Lebedew used very thin strips of platinum and worked at extremely low pressure. Nichols and Hull used rather higher pressure (about 16 mm.) where the radiometer action was found to be minimum, and eliminated it by differential readings from the two sides. The receiving glass disc had one surface silvered, so that this silvered surface was always heated whether the radiation was incident on this surface or on the other surface. When the radiation fell on the silvered surface, the radiation pressure and radiometer action assisted each other while in the other case they were opposed. Hull later placed the silvered side of a thin cover glass in contact with the blackened side of a similar glass and the whole was enclosed in a cell of two thin glass plates which were separated from these by air space. Thus both the surfaces of the cell were equally heated and the radiometer action was practically eliminated. Rocket action was eliminated since no gas left the cell. The senior author and Chakravarti[1] devised a simple arrangement on similar lines. Their vanes were constructed as follows :—The silvered sides of two thin circular glass slides (as used for microscopical studies) were put one upon the other and connected to each other by a trace of canada-balsam on the fringes, thus enclosing a thin film of air in between. When light, previously filtered of all rays capable of heating glass, is allowed to fall on one side of this vane, the two sides of the film are instantly raised to the same temperature (because it is extremely thin), and hence the radiometer action is eliminated. Two such vanes were suspended on the opposite arms of a torsion balance which is suspended by a thin quartz fibre (Fig. 12) having a mirror m inside a vessel that can be evacuated. On account of the low pressure convection currents are absent. The rocket action is also eliminated since the liberated gas remains inside the system, and the action and reaction being equal, the net effect is zero.

If p is the pressure exerted by radiation on a vane, A the area of the vane, $2d$ the distance between the two vanes, the turning moment exerted by the radiation is pAd. This must equal $\mu\theta$ where μ is the torsional couple per unit twist and θ the steady deflection produced.

Hence
$$p = \frac{\mu}{Ad}\,\theta.$$

μ can be obtained from observations of the period of free oscillation of the system if its moment of inertia be known, and θ is measured by the lamp and mirror arrangement. It was found that the pressure was approximately equal to I/c, *i.e.*, the energy density of incident radiation.

15·21. Total Radiation from a Black Radiator. The Stefan-Boltzmann Law.

—In 1879 J. Stefan deduced empirically from the experimental data of Tyndall and of Dulong and Petit that the total radiation from any heated body is proportional to the fourth power of its absolute temperature. In 1884 Boltzmann[2] gave a theoretical proof of the law based on thermodynamical considerations. He showed that the law applies strictly to emission from a black body. The law is therefore generally known as the *Stefan-Boltzmann law*, and may be formally enunciated as follows :—*If a black body at absolute temperature* T

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[1] *Journal of Asiatic Society of Bengal*, **14**, 425, 1918.

[2] *Wied. Ann.*, **22**, 291, 1884.

be surrounded by another black body at absolute temperature T_0, *the amount of energy E lost per second per square centimetre of the former is*

$$E = \sigma(T^4 - T_0^4). \qquad \qquad (17)$$

For proving this law, we consider radiation in a black body chamber, and try to apply thermodynamical laws to the radiation. Let u denote the energy density of radiation inside the enclosure, V its total volume and p the pressure of radiation. Then both u and p are simply functions of the absolute temperature T. We have further the total energy U of radiation $=uV$.

We apply[1] equation (15) of p. 329 connecting U, V and p. We have

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p, \qquad \qquad (18)$$

and

$$\frac{\partial U}{\partial V} = u, \quad p = \frac{u}{3},$$

since the radiation is diffuse (equation 11).

Hence equation (18) reduces to

$$u = \frac{T}{3}\frac{\partial u}{\partial T} - \frac{u}{3}, \qquad \text{or } \frac{du}{u} = 4\frac{dT}{T};$$

or

$$u = aT^4, \qquad \qquad (19)$$

where 'a' is a constant, independent of the properties of the body.

This gives us the density of radiation in the enclosure. The amount of energy lost through an aperture of unit area per second is, from equations (19) and (10), given by

$$H = \pi K = \frac{cu}{4} = \frac{ac}{4}T^4 = \sigma T^4. \qquad \qquad (20)$$

'σ' is known as Stefan's constant. The value of 'σ' has been found to be $5 \cdot 7 \times 10^{-5}$ ergs sec.$^{-1}$ cm.$^{-2}$ °K^{-4}.

15·22. Experimental Verification of Stefan's Law.— The law was subjected to experimental test by various investigators. Lummer and Pringsheim[2] investigated the emission from a black body over the range of temperature 100°C to

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[1] Boltzmann deduced the law by imagining the radiation to perform a Carnot cycle. He utilised the conceptions of Bartoli. This is however unnecessary here for we have shown black radiation to be analogous to a gas and we can proceed directly to apply the general thermodynamical laws to black radiation.

[2] *Wied. Ann.*, **63**, 395, 1893.

1260°C and found the law to hold true within experimental errors. We give below a brief account of their apparatus and arrangement.

A is a hollow vessel containing boiling water (Fig. 13) which acts as the standard source of radiation for calibrating the bolometer B from time to time. The black body C, employed for the range of temperatures 200°C to 600°C consisted of a hollow copper sphere blackened inside with platinum black, and placed in a bath of a mixture of sodium and potassium nitrates which melts at 219°C. This salt bath could be maintained at any desired temperature. The temperature could be measured with a thermo-element T.

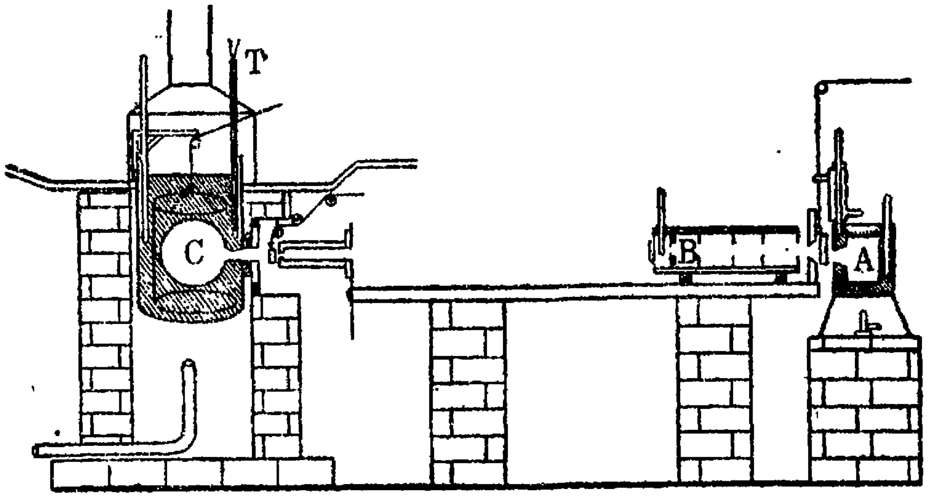

Fig. 13.—Lummer and Pringsheim's apparatus for verifying Stefan's Law.

For temperatures between 900°C and 1300°C the black body shown in Fig. 14 was employed. D is an iron cylinder coated inside with platinum black and enclosed in a double-walled gas furnace. The temperature inside the iron cylinder was obtained by a thermo-element enclosed in a porcelain tube passing through the furnace.

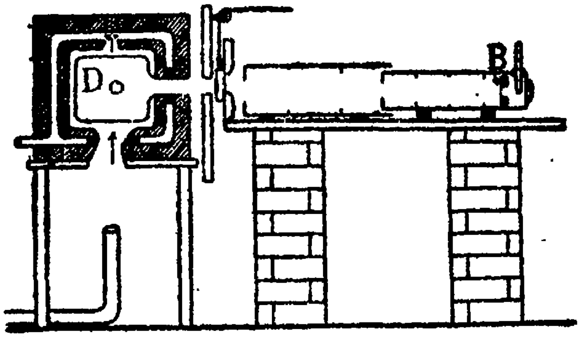

Fig. 14.—Black body for temperatures between 900° and 1300°C.

The measuring instrument shown at B was the surface bolometer of Lummer and Kurlbaum. A description of this as well as the method of connecting it will be given later in this chapter. Besides, there are a number of water-cooled shutters so that radiation can be stopped or allowed to fall at will.

The procedure adopted was as follows :—The bath was heated up to the desired temperature and maintained steady, and then the shutter was raised to allow radiation from C to fall on the bolometer and the maximum deflection registered by the galvanometer noted. The bolometer was kept at different distances from the black body and the inverse square law verified. Next observations were taken with the black body at different temperatures. The observations were all reduced to a common arbitrary unit depending on the radiation from the black body A at 100°C and at a distance of 633 mm. If d represents the deflection of the galvanometer needle, T the absolute temperature of the black body, 290°K the temperature of the shutter protecting the bolometer, then

$$d = a\,(T^4 - 290^4)$$

from Stefan's law. a was found to be constant whose mean value for the instrument was $123{\cdot}8 \times 10^{-10}$. Hence the truth of Stefan's law is established.

15·23. A Simple Method of determining σ.

—Kussmann[1] has given a laboratory method of determining σ by making use of the radio-micrometer. His apparatus is diagrammatically represented in Fig. 15.

A is the black body whose temperature is given by the thermocouple Th, S is a shutter, and D a water-cooled diaphragm. Radiation from A travelling through G falls on R which consists of a very thin blackened strip of manganin or constantan. The strip becomes heated and acquires a steady final temperature. It also emits radiation which is concentrated by the lens L and falls on the radio-micrometer[2] M, producing a steady deflection. Next the radiation from the

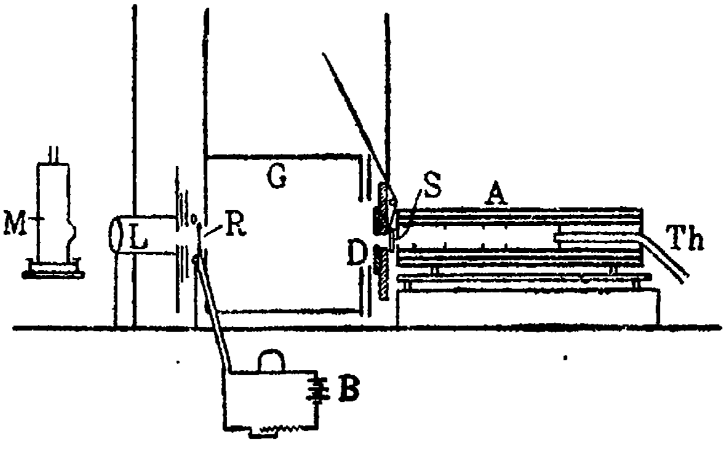

Fig. 15.—Kussmann's apparatus for determining σ.

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[1] *Zeits. f. Physik*, **25**, 58, 1924.

[2] This instrument is described in detail in sec. 15·41.

black body is cut off and the strip heated electrically[1] by means of the battery B. The electrical power supplied is so adjusted as to produce the same deflection as before. Then we can equate the amount of energy supplied to the strip by radiation from A to the electrical energy supplied. Thus if i be the current in amperes through the strip, R its resistance, T_1, T_2 the temperatures of the black body and the shutter, A_1, A_2 the areas of the strip and the diaphragm respectively, r the distance between the diaphragm and the strip, then the energy received by the plate by radiation

$$= \frac{EA_1A_2}{r^2}\,a = \frac{A_1A_2}{\pi r^2}\,\sigma(T_1^4 - T_2^4)a,$$

where a is a correction factor necessitated by the diffuse reflection from the strip, atmospheric absorption etc.

Equating this to the electrical energys supplied to the plate we have

$$i^2\text{R} = \frac{A_1A_2}{\pi r^2}\,(T_1^4 - T_2^4)a.$$

$$\therefore \sigma = \frac{i^2\text{R}.\ \pi r^2}{A_1A_2(T_1^4 - T_2^4)a}\,\frac{\text{watts}}{(\text{cm}^2)\ (\text{degree})^4}. \qquad (21)$$

As a result of numerous determinations Kussmann gives the corrected value of σ as $5{\cdot}79\times10^{-12}$ watts/cm.^{2} °K^4.

15·24. Critical Review of the Experimental Work on the Determination of the Stefan Constant.—The value of the Stefan constant has been determined by a large number of workers. We may mention here a few of them, *viz.*, Lummer, Kurlbaum, Valentiner, Féry, Gerlach, Coblentz and Müller. A very good account of their work will be found in *Handbuch der Experimental-physik*, Vol. 9, pp. 423-455. We shall consider bery briefly the work of Coblentz and Müller for they took great care and obtained good values.

Coblentz[2] employed as a receiver of radiation a modified Ångström pyrheliometer containing a thin blackened manganin strip, behind which but close to it a thermopile was placed. The incident radiation was absorbed by the strip which in turn radiated to the thermopile producing a deflection. Next the strip was heated electrically to produce the same deflection. In this way σ could be calculated. Coblentz employed various corrections and got the value $\sigma = 5{\cdot}72\times10^{-12}$ watts.

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[1] The idea of determining 'σ' by comparison of radiant energy with electrical energy was first given by Kurlbaum who however used a bolometer. He got the value $\sigma = 5{\cdot}32\times10^{-12}$ watts which is too low.

[2] *Bull. Bur. of Stand.*, **12**, 503, 1916; **15**, 529, 1923. A good account of this work as well as of other determinations will be found in *A Dictionary of Applied Physics*, Vol. 4, article by Coblentz.

Müller[1] performed a series of experiments with great care and claims an error of less than ·5% for his result. He employed rather large-sized plates of Ni or Pt as receiver which was placed at the centre of a hollow hemisphere as in the Ångström pyrheliometer. Thus the radiation was received under almost perfect black-body conditions. The strip in turn radiated to a surface bolometer. Due to the large size of the plate, the uncertainty in its determination was reduced to a minimum. The compensation method was employed to determine the energy received by the plate in absolute measure. Corrections were applied for the lack of blackness of the radiator, for the imperfect absorption of the receiving strip, for the loss of radiation due to water vapour and carbon dioxide in the air, etc. He got the mean value from a number of determinations to be $5{\cdot}774 \times 10^{-12}$ watt $\text{cm}^{-2}\,{}^\circ\text{K}^{-4}$.

It is rather unsatisfactory to find that the values obtained by different observers vary rather widely from $5{\cdot}32 \times 10^{-12}$ to $6{\cdot}15 \times 10^{-12}$. Some Investigators[2] have even expressed doubt as to whether σ can be regarded as a constant over the whole range of temperature. Birge[3] has given a critical discussion of these experimental works and adopts the mean value $5{\cdot}672 \times 10^{-12}$. The results of the most reliable direct determinations have been compiled by R. Ladenberg[4] and are given in Table 1. Ladenberg in 1933 put down the mean value as $5{\cdot}767$. Wensel[5] from a critical examination of the direct determinations arrives at the value $\sigma = 5{\cdot}69 \times 10^{-12}$.

Table 1.—*Recent determinations of* σ.

Authors[6]		Value of σ
W. Gerlach (1916).	..	$5{\cdot}80 \times 10^{-12}$ watt cm^{-2} deg.^{-4}
W. W. Coblentz (1911)	..	$5{\cdot}722$
K. Hoffmann (1923)	..	$5{\cdot}76$
A. Kussmann (1924)	..	$5{\cdot}795$
F. Hoare (1928) (1932)	..	$5{\cdot}737$
C. F Mendenhall (1929)	..	$5{\cdot}79$
C. Müller (1929)	..	$5{\cdot}77$

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[1] *Zeits. f. Instrk.*, **44**, 119, 1923; *Zeits. f. Physik*, **52, 1**, 1933.

[2] Sturm, *Zeits. f. Physik*, **51**. 287, 1928; Kothari and Majumdar, *Ibid.* **60**, 250.

[3] *Rev. Mod. Phys.*, 2, 56, 1930; *Ibid*, **13**, 233, 1941.

[4] See *Handbuch der Physik*, (2nd Ed.) Vol. 23 (I) p. 20, 1933.

[5] *Bull. Res. Bur. Stand.*, **22**, 375, 1939.

[6] Gerlach, *Ann. d. Physik*, **38**, 1, 1912; **50**, 259, 1916.
Hoffmann, *Zeits. f. Physik*, **14**, 315, 1923.
Hoare, *Phil Mag.*, **6**, 828, 1928; **13**, 380, 1932.
Mendenhall, *Phys. Rev.*, **34**, 502, 1929.

DISTRIBUTION OF ENERGY IN THE SPECTRUM EMITTED BY A BLACK BODY

15·25. Adiabatic Expansion of Radiation. Wien's Displacement Law.—We have seen that the radiation emitted by a body is not confined to a single wavelength but is spread over a continuous spectrum. We shall now consider how energy is distributed over the different wavelengths. Considered from the quantum theory of light, the problem reduces to finding out how many quanta having the energy value between ϵ and $\epsilon + d\epsilon$ (frequency ν and $\nu+d\nu$) are contained per unit volume in a black body chamber at temperature T. The problem is thus analogous to that of distribution of energy amongst molecules, but it did not present itself in this form to the early workers before the rise of the quantum theory. They worked on the lines of classical thermodynamics and the electromagnetic theory of radiation and arrived at a complete solution of the problem in several stages in a somewhat laborious fashion. The first step was taken by Wien[1] who showed in 1893 that $E_\lambda\, d\lambda$, *i.e.*, amount of energy contained in the spectral region included within the wavelengths λ and $\lambda+d\lambda$ emitted by a black body at temperature T, is of the form

$$E_\lambda\, d\lambda = \frac{A}{\lambda^5} f(\lambda T)\, d\lambda, \quad . \quad . \quad . \quad . \quad (22)$$

where A is a constant and $f(\lambda T)$ is a function of the product (λT).

(*i*) This expression was obtained from purely thermodynamical reasoning. For this purpose let us think of an imaginary experiment (Gedanken versuch) performed with a spherical[2] enclosure having perfectly reflecting walls which are made of elastic material and are capable of slowly moving outwards. Let the enclosure be maintained at some temperature T and let a small speck of black body (carbon) of negligible heat capacity be placed inside it. In a short time the radiation inside the enclosure will be in equilibrium with the black body. Now we take out the black body so that the enclosure remains filled up with diffuse radiation at T°.

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[1] *Berl. Ber.* (1893), p. 55; *Wied. Ann.*, **52**, 132, 1894.

[2] By an extension of these arguments it can be shown that these results will hold for an enclosure of any shape whatsoever. See Planck, *Wärmestrahlung.*

Next allow the black radiation within the enclosure to expand adiabatically. This may be brought about by supposing that the walls suddenly begin to move outwards slowly with the uniform velocity v ($v \lll c$). When the volume has expanded to a certain extent (V') the temperature will fall say to T' and the quality of radiation may also change. But it can be proved that the radiation remains black radiation characteristic of the lower temperature T'.

If this were not the case, let us assume provisionally that the energy, though of the same density, is not of the same quality as the black radiation at temperature T'. For fixing our ideas we may suppose that the red is in excess and the blue is in defect. Now let us insert substances A and B, absorbing red and blue rays respectively. Then A will be more heated, and B will be cooled. By working a Carnot engine between them we convert excess heat in A to work and can bring the quality to that of full radiation. The temperature will be lowered below T' because some energy has been converted to work. Now remove the red and the blue bodies and compress the enclosure adiabatically till it attains the original volume. The temperature at the end of this process will be less than T. Again by the previous supposition we do not have full radiation, and by inserting absorbing bodies and working a Carnot cycle, the temperature can be lowered till the quality is full (black). Hence finally the original volume becomes colder while some work is obtained during the whole process. Thus we are able to get work continuously by using the heat of a single body (the reservoir) without having to maintain any body at a lower temperature; this is against the second law. Hence the assumption upon which the deduction is based is not true. We must suppose that full radiation after adiabatic expansion remains full, characteristic of the lower temperature.

(*ii*) Next we must calculate the change in frequency due to Doppler effect which every wave will suffer on reflection at the moving wall. The waves inside the enclosure will be incident on the walls at all angles. In the case of normal incidence we know that a particular wave of frequency[1] ν will be changed, according to Doppler principle, to $\nu(1-v/c)$ on reaching the wall. The frequency of the reflected wave is again decreased in the ratio $1 : 1/(1+v/c)$, for now the source itself is in a state of motion. The resultant frequency

$$\nu+d\nu = \frac{\nu(1-v/c)}{(1+v/c)} = \nu\left(1-\frac{2v}{c}\right), \qquad (23)$$

since v/c is small, or

$$\frac{d\nu}{\nu} = -\frac{2v}{c}; \text{ or } \frac{d\lambda}{\lambda} = \frac{2v}{c}. \qquad (24)$$

When however the wavefront is incident obliquely so that the normal to it makes an angle θ with the normal to the surface, (Fig. 16) the effective part of v is that perpendicular to the wavefront, *i.e.*, $v \cos \theta$, and therefore

$$d\lambda = \frac{2v\cos\theta}{c}\lambda. \qquad (25)$$

Waves will be incident on the walls of the surface in all possible directions and will suffer a change in wavelength. Consider a wave of length λ incident at an angle θ with the normal. At each reflection the change in wavelength is given by (25).

Between successive reflections the wave travels a distance $2r \cos \theta$ (Fig. 17) and hence the number of reflections per second

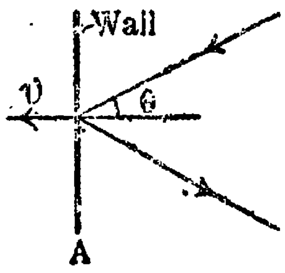

Fig. 16.—Oblique incidence.

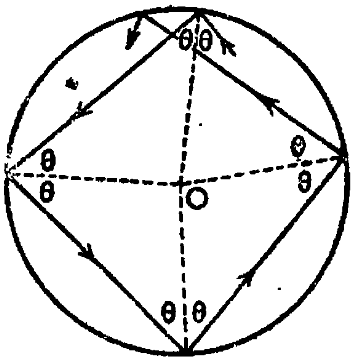

Fig. 17.—Change in wavelength on reflection at the wall.

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[1] We can deduce the same expression from the Quantum Theory of Radiation. Consider any photon incident upon the walls of the enclosure. The moment of a photon $= h\nu/c$. The number of photons striking the moving reflector per second per unit area of its surface $= n(c-v)$ where n is the number of photons per c.c. in the incident beam.

is $c/2r \cos\theta$. Hence the change of wavelength per second is

$$d\lambda = \left(\frac{c}{2r\cos\theta}\right)\left(\frac{2v\cos\theta}{c}\right)\lambda = \frac{v\lambda}{r};$$

or

$$\frac{d\lambda}{\lambda} = \frac{v}{r} = \frac{\delta r}{r}, \qquad . \quad . \quad . \quad . \quad . \qquad (26)$$

where $v = \delta r$ the distance traversed in 1 sec.

(*iii*) The temperature of the enclosure is also changed. For we started with a given amount of energy, but this energy is now distributed over a larger volume and a part of it is spent in doing external work (*i.e.*, the work done by the pressure of radiant energy upon the walls). Since the process is an adiabatic one we have

$$\delta Q = dU + pdV = 0,$$

where dU is the total change in internal energy and pdV is the work done by radiant energy. Now $U = uV$ where u is the density of radiation and V the volume of the sphere. Also $p = u/3$. Hence

$$d(uV) + \frac{u}{3}dV = 0,$$

or

$$\frac{du}{u} + \frac{4}{3}\frac{dV}{V} = 0.$$

On integration, we get

$$uV^{4/3} = \text{constant}. \qquad . \quad . \quad . \quad . \quad . \qquad (27)$$

This can also be written in the form $pV^{4/3} = \text{constant}$ for an adiabatic process. Thus radiation behaves like a gas having its $\gamma = 4/3$.

Let the initial frequency of radiation be ν and the final frequency ν'. Therefore the change in momentum suffered by a photon $= (h/c)(\nu+\nu')$. Hence the pressure p exerted on the wall, which is equal to the change in momentum per second, is equal to $(h/c)(\nu+\nu').n(c-v)$. Therefore the work done per second on the moving wall, *i.e.*, energy imparted by the $n(c-v)$ photons $= pv = (h/c)(\nu+\nu').\ n(c-v).\ v$. Hence the work done by each photon $= (h/c)(\nu+\nu')v$. This will produce a change in the energy of the photon. Hence

$$h(\nu'-\nu) = -\frac{h}{c}(\nu+\nu')v.$$

$$\text{Or } 1 + \frac{2\nu}{\nu'-\nu} = -\frac{c}{v}; \text{ or } \frac{d\nu}{\nu} = -\frac{2v}{c+v} = -\frac{2v}{c}.$$

Now $u = aT^4$ from Stefan's law and $V = \frac{4}{3}\pi r^3$. Hence (27) yields

$$rT = \text{const.} \qquad (28)$$

Therefore

$$\frac{dT}{T} = -\frac{dr}{r}. \qquad (28a)$$

Combining with (26) we get

$$\frac{d\lambda}{\lambda} = -\frac{dT}{T},$$

or

$$\lambda T = \text{constant}. \qquad (29)$$

Thus if radiation of a particular wavelength at a certain temperature is adiabatically altered to another wavelength, then the temperature changes in the inverse ratio.

(*iv*) We shall next prove that $u_\lambda \lambda^5 = \text{const.}$ *i.e.*, the density of radiation is changed inversely as λ^5 in the above process, for suppose we isolate waves of wave-length lying between λ and $\lambda + d\lambda$ in the spherical chamber, and subject these alone to an adiabatic expansion. The work done in the adiabatic expansion is $\frac{1}{3}u_\lambda\, d\lambda . \Delta V$, and this should be equal to the decrement in the total energy content, *viz.*, $-\Delta(u_\lambda\, d\lambda .\, V)$. Hence

$$\tfrac{1}{3}u_\lambda \,.\, d\lambda . \Delta V = -\Delta(u_\lambda\, d\lambda . V).$$

Now $d\lambda$ changes in the same way as λ, hence $\frac{\Delta d\lambda}{d\lambda} = \frac{\Delta\lambda}{\lambda}$, and $V \propto \lambda^3$ from (26). Hence rearranging[1], we have

$$\frac{5\Delta\lambda}{\lambda} + \frac{\Delta u_\lambda}{u_\lambda} = 0,$$

or

$$u_\lambda \lambda^5 = \text{constant} = u_\lambda' \lambda'^5, \qquad (30)$$

where u_λ' is the density of the radiation λ' to which λ has been transformed by the expansion. This will correspond to the equilibrium radiation-density at the temperature $T' = \lambda T/\lambda'$.

Obviously u_λ must be a function of T, hence the constant in (30) must involve T. But the constant is such that it remains constant throughout such adiabatic alteration of wavelength. We

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[1] The steps are:—

$$\tfrac{1}{3}u_\lambda\, d\lambda\, \Delta V = -\Delta u_\lambda\, d\lambda . V - u_\lambda\, \Delta d\lambda . V - u_\lambda\, d\lambda . \Delta V.$$

Dividing by $u_\lambda\, V .\, d\lambda$ we have

$$\tfrac{1}{3}\frac{\Delta V}{V} = -\frac{\Delta u_\lambda}{u_\lambda} - \frac{\Delta d\lambda}{d\lambda} - \frac{\Delta V}{V}.$$

Now put

$$\frac{\Delta V}{V} = \frac{3\Delta\lambda}{\lambda}, \quad \frac{\Delta d\lambda}{d\lambda} = \frac{\Delta\lambda}{\lambda}.$$

have seen above that the quantity λT is a constant for this process. Clearly therefore this constant is a function of the product λT. We can therefore put

$$u_\lambda\, d\lambda = \frac{A}{\lambda^5}\cdot f(\lambda T) d\lambda. \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

If the frequencies ν and $\nu + d\nu$ correspond to the wave-lengths λ and $\lambda + d\lambda$ and $u_\nu\, d\nu$ represents the energy in this frequency interval, we have

$$u_\nu\, d\nu = u_\lambda\, d\lambda,$$

and $$\lambda = \frac{c}{\nu}, \quad d\lambda = -\frac{c}{\nu^2}\, d\nu.$$

Combining these with (31) we get

$$u_\nu\, d\nu = B\nu^3 \phi\left(\frac{\nu}{T}\right) d\nu. \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

We can also write

$$u_\lambda\, d\lambda = AT^5\, F(\lambda T)\, d\lambda,$$

where $$F(\lambda T) = (\lambda T)^{-5}\, f(\lambda T).$$

The emission E_λ is proportional to the energy density u_λ. It follows that

$$\frac{E_\lambda}{E_\lambda'} = \left(\frac{T}{T'}\right)^5. \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

It is now apparent that if the distribution at any temperature T be given the distribution at a second higher temperature T' can be obtained graphically, by shortening the abscissa in the ratio of T/T' (Fig. 18) and increasing the corresponding ordinate in the ratio $(T'/T)^5$. The wave interval $d\lambda$ also becomes shortened in the ratio T/T'. The curve now becomes higher but more closed up and the total area which represents the intensity is changed in the ratio $(T'/T)^4$. Corresponding to point P of maximum emission in the first curve there is a point P', of maximum emission in the second such that

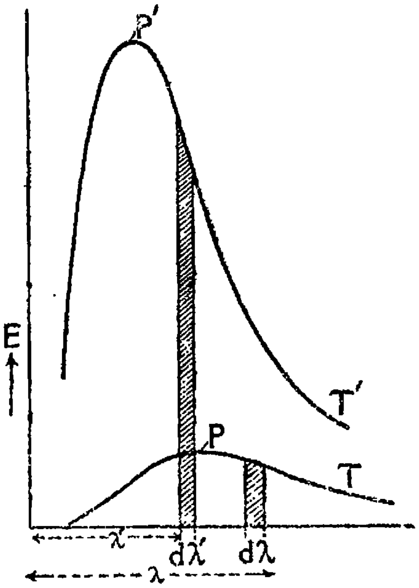

Fig. 18.—Correspondence of blackbody curves for two temperatures.

$$\lambda_m T = \lambda_m' T' = b = \text{const.}, \quad . \quad . \quad . \quad . \quad (34)$$

where λ_m is the wavelength corresponding to the maximum emission. The constant b is the root of the equation

$$\frac{dE_\lambda}{d\lambda} = 0.$$

We obtain for the corresponding emissions the relation

$$\frac{E_m}{E_m'} = \left(\frac{T}{T'}\right)^5 \quad . \quad . \quad . \quad . \quad . \quad (35)$$

15·26. Experimental Verification.—These important deductions from Wien's displacement law were subjected to a series of experimental tests by Paschen,[1] Lummer and Pringsheim,[2] Rubens and Kurlbaum. We give below a short description of the experiment and results of Lummer and Pringsheim (1899). They used radiation from an electrically heated carbon tube and produced the spectrum by refraction through a fluorspar prism. Corrections were applied to convert the prismatic spectrum into a normal one by means of the known dispersion curve of fluorspar. The distribution of energy was measured by means of a Lummer-Kurlbaum linear bolometer which was enclosed in an air-tight case for diminishing the absorption due to water vapour and carbon dioxide. The distribution of energy in the spectrum for various temperatures between 621 and 1646°K. was obtained and curves plotted (Fig. 19). The

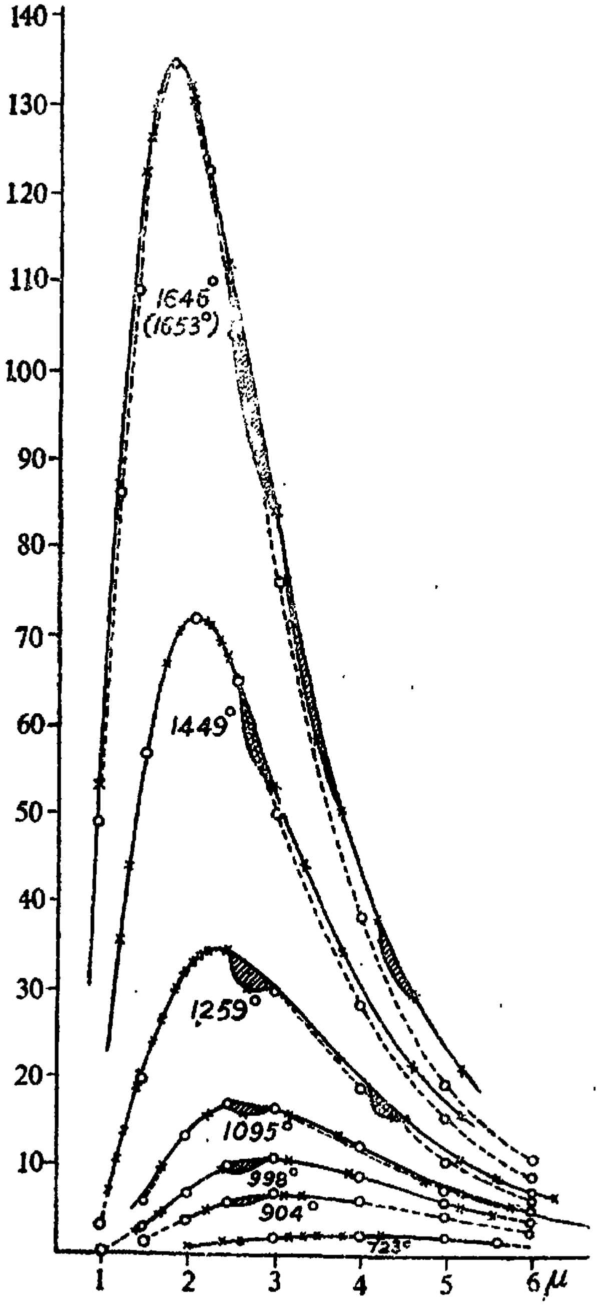

Fig. 19.—Distribution of energy in the spectrum of a black body

ordinates represent emissive powers and the abscissæ wavelengths. The full lines denote the curves obtained experimentally while the dotted lines represent the curves calculated from Wien's Distribution Law (sec. 15·29). The total radiation at a temperature is represented by the area enclosed between the curve and x-axis, and varies as T^4. The small patches of shaded area represent the absorption bands of carbon dioxide and water vapour. The absorption of fluorspar begins at 6μ where the curves are seen to end abruptly. Of any two curves that corresponding to the higher temperature always lies outside that corresponding to the lower temperature. The wavelength of maximum emisssion shifts towards the origin as the temperature rises. From these curves the values of E_m and λ_m could be read The experimental results are given in Table 2.

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[1] *Wied. Ann.*, **60**, 662, 1897; *Ann. d. Physik*, **4**, 277, 1901.

[2] *Verh. d. D. Phys. Ges.*, **1**, 213, 1899.

The table shows clearly the validity of the results (34) and (35). If the value of b or $E_m T^{-5}$ be known these laws enable us to determine the temperature of any substance (assumed to be a black body) if λ_m or E_m can be found from experimental work. The value of b is seen to be 0·294 cm.× degrees and that of $E_m T^{-5}$ to be 2·188×10^{-14} ergs×degree. More accurate experiments described in §15·37 show that $b = 0{\cdot}288$ cm.×degree.

Table 2. Experimental Verification of Wien's Displacement Law.

Temp. °K	λ_m in μ's	E_m	$\lambda_m T$ in micron-degrees	$E_m T^{-5}$ $\times 10^{17}$
1646	1·78	270·6	2928	2246
1460·4	2·04	145·0	2979	2184
1259·0	2·35	68·8	2959	2176
1094·5	2·71	34·0	2966	2164
998·5	2·96	21·5	2956	2166
908·5	3·28	13·66	2980	2208
723·0	4·08	4·28	2950	2166
621·2	4·53	2·026	2814	2190
			Mean=2940	2188

This furnishes us with a simple method of determining the temperature of all radiating bodies including those in the heavens. Thus for the moon, $\lambda_m = 14\mu$ and hence $T = \dfrac{\cdot 288}{14\times 10^{-4}} = 200°\text{K}$. Similarly we can calculate the temperature of the sun (see §15·55).

INVESTIGATION ON THE FORM OF $f(\lambda T)$. COMPLETE LAW OF SPECTRAL DISTRIBUTION OF ENERGY.

15·27.—Nothing further can be obtained from thermodynamical considerations in trying to determine the form of $f(\lambda T)$, since all the thermodynamic conditions are satisfied by any continuous function f. Hence, as in the determination of the law of distribution of velocities of a perfect gas, pure thermodynamics is of no further use in solving the problem and we must invoke the help of other principles. Some of the earlier attempts are described below.

15·28. The Rayleigh-Jeans Law.—The first attempts on classical lines in this direction were made by Lord Rayleigh and were completed by J. H. Jeans.

At the time when Lord Rayleigh took up the investigation, the prevalent idea was that radiation consisted of vibrations in an all-pervading continuous medium called "æther" (luminiferous æther) whose motions were governed by Maxwell's equations connecting the electric and magnetic vectors (equations of æther). Maxwell had shown, with the aid of these equations, that light is an electro-magnetic vibration in this medium, the electric and magnetic vectors being perpendicular to each other, and perpendicular to the direction of the ray. This result comes out as a solution of the Maxwell equations, and will be found in any text-book on Electromagnetism[1]. Let us now see how this conception of radiation can be applied to the present investigation. The black body chamber is filled with diffuse radiation of all frequencies between 0 and ∞, and the first problem before Lord Rayleigh was to find out the number of the possible wave-motions of æther having their frequency between ν and $\nu+d\nu$.

A very simplified way of doing this is as follows:—Consider a black body chamber in the form of a rectangular parallelopiped having the sides p, q, r with perfectly reflecting walls, and let us place inside this a black particle. In course of time the enclosure will be filled with stationary waves of all lengths, for the particle emits radiation which is reflected back by the walls. The reflected and incident waves interfere and stationary waves are formed. This is clear from an acoustic analogy. If we have a wire fixed

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[1] See for example, Jeans' *Electricity and Magnetism*.

at both ends and pluck it at one point, waves run to and fro and ultimately stationary waves are formed whose nodes are at the fixed ends. The wire may vibrate in one segment producing the fundamental tone or it may vibrate in several segments producing overtones (wavelength $2l/n$) where n is any positive integral number.

We can apply the same analogy to the waves of radiant energy which run perpendicular to the walls of the parallelopiped. Here also stationary waves are formed whose nodal[1] planes are the boundary walls and planes parallel to them and separated by a distance $\lambda/2$.

But in general the radiation is diffuse, *i.e.*, the rays can be inclined at any angle to the rectangular axes. Let us take a ray incident on the mirror as indicated in Fig. 20 and having the direction cosines α, β, γ. We have

$$\alpha^2+\beta^2+\gamma^2=1. \qquad (36)$$

By reflection at the several walls the ray will be transformed into eight reflected rays having the direction cosines

$$\pm\alpha,\ \pm\beta,\ \pm\gamma.$$

Let us first treat the reflection on the surface YOZ. The interference of the incident and reflected waves will produce a system of stationary waves.[2] The distance between successive nodal planes is given by

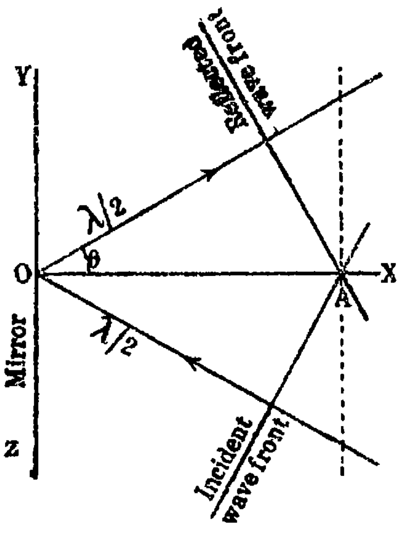

Fig. 20.—Formation of stationary waves.

$$x=\lambda/2\alpha.$$

This formula readily follows from Fig. 20. The two waves interfere at the point A and if A is a node, we have, remembering that O is a node, the relation

$$\mathrm{OA}=\frac{\lambda}{2\cos\theta}=\frac{\lambda}{2\alpha}.$$

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[1] For electromagnetic waves, assuming metallic reflection, there will be a node of the electric vector E at the walls. For the following computation it is immaterial whether there is a node or antinode at the wall, depending upon the nature of the wall.

[2] This can be easily shown from the electromagnetic theory.

If the opposite surface $x=p$ is a nodal plane, we have

$$p=\frac{n_1\lambda}{2\alpha}, \qquad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

where n_1 is an integer.

In the same way we can prove that for reflection at the surfaces perpendicular to OY and OZ we have

$$q=\frac{n_2\lambda}{2\beta},\ r=\frac{n_3\lambda}{2\gamma}. \qquad . \quad . \quad . \quad . \quad . \quad (37a)$$

Every possible system of waves in the parallelopiped is given by a combination of the three integral numbers which gives us the number of nodal surfaces perpendicular to any co-ordinate axis. The electric and magnetic field which characterise the state of the oscillations is given by expressions of the form

$$\begin{matrix}\cos\\ \sin\end{matrix}\left(\frac{n_1\pi x}{p}\right)\ \begin{matrix}\cos\\ \sin\end{matrix}\left(\frac{n_2\pi y}{q}\right)\ \begin{matrix}\cos\\ \sin\end{matrix}\left(\frac{n_3\pi z}{r}\right)\times\{a\cos 2\pi\nu t+a'\sin 2\pi\nu t\}.$$

It was shown by Jeans[1] that these expressions are solutions of Maxwell's equations which satisfy the boundary conditions in the black body chamber.

When we form the total expression for the electric and magnetic field of oscillations, we obtain two solutions which represent the two states of polarisation perpendicular to each other. Therefore every combination of integral values of n_1, n_2, n_3 gives us two characteristic oscillations having the common frequency ν.

Combining (36), (37) and (37*a*) we get

$$\frac{n_1^2}{p^2}+\frac{n_2^2}{q^2}+\frac{n_3^2}{r^2}=\frac{4}{\lambda^2}=\frac{4\nu^2}{c^2}. \qquad . \quad . \quad . \quad . \quad (38)$$

Equation (38) represents an ellipsoid with n_1, n_2, n_3 in place of x, y, z as the co-ordinate axes. Any combination of n_1, n_2, n_3 will represent a mode of vibration. Since n_1, n_2, n_3 can have only integral values it is evident that all possible combinations of these will be simply given by the number of points formed by the intersection of the parallel lines drawn through successive integral values of n_1, n_2, n_3. These points clearly occur at the rate of one per unit volume, hence their number will be simply given by the volume of the ellipsoid. Further as only positive values of n_1, n_2, n_3 are permissible and these occur only in one out of the eight octants, the possible modes of vibration of frequency lying between 0 and ν are given by 1/8th of the volume of the ellipsoid which is $(4\pi/3)\times 8pqr\times \nu^3/c^3$. Similarly the number of vibrations between the frequencies ν and $\nu+d\nu$ is equal to 1/8th of the volume of the ellipsoidal shell formed between the parameters ν and $\nu+d\nu$ and is equal to

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[1] See Jeans, *Electricity and Magnetism.*

$$\frac{1}{8}\frac{\partial}{\partial\nu}\left[\frac{4\pi}{3}pqr\frac{8\nu^3}{c^3}\right]d\nu = 4\pi V\frac{\nu^2}{c^3}\,d\nu, \quad . \quad . \quad . \quad (39)$$

where $V=pqr=$volume of the enclosure. Thus the number of vibrations per unit volume is

$$\frac{4\pi\nu^2 d\nu}{c^3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (39a)$$

and is independent of the volume of the enclosure. We have proved this result with respect to a rectangular enclosure but it was shown by Weyl that so long as the wavelength of the vibration is small compared with the size of enclosure the foregoing result holds whatever be the shape or size of the enclosure. Born proved the same result for a crystalline body.

As mentioned above the waves in æther are transverse and can be polarised, and each polarised component is independent of the other, we must therefore double the number. Hence the required number is

$$\frac{8\pi\nu^2 d\nu}{c^3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (39b)$$

Converting frequency into wavelengths (since $\nu=c/\lambda$), the number becomes $(8\pi/\lambda^4)d\lambda$ per unit volume.

The argument by which we have counted up the number of independent free vibrations holds for any elastic medium.

The number of independent free vibrations in æther being counted up, the problem of finding out the partition of energy becomes quite simple. For from the dynamics of the medium, the energy of each vibration is given by expressions of the type

$$E = \tfrac{1}{2}a\phi^2 + \tfrac{1}{2}b\dot{\phi}^2,$$

where a and b are constants and ϕ represents the displacement. Each vibration thus contributes two squared terms to the energy of the whole system. The energy of each vibration is therefore equal to kT from the equipartition law, where k is the Boltzmann constant and T is the temperature of the radiation. This temperature is the temperature of a material body say a gas which would remain in equilibrium with that radiation. Hence the energy density of wavelength lying between λ and $\lambda+d\lambda$ in the enclosure is given by

$$u_\lambda \, d\lambda = \frac{8\pi}{\lambda^4} kT \, d\lambda. \qquad . \quad . \quad . \quad . \quad . \quad (40)$$

and the intensity of emission

$$E_\lambda = \frac{cu_\lambda}{4\pi} = \frac{2c}{\lambda^4} kT. \qquad . \quad . \quad . \quad . \quad . \quad (40a)$$

15·29. Wien's Radiation Formula.[1]—Wien[2] on the other hand made some arbitrary assumptions regarding the mechanism of emission and absorption. He assumed that the radiation inside a hollow enclosure may be supposed to be produced by a resonator of molecular dimensions and that the frequency of the wave emitted is proportional to the kinetic energy of the resonator; *i.e.*,

$$\tfrac{1}{2}mv^2 = a\nu = ac/\lambda,$$

where a is a constant and ν is the frequency of the light emitted. It is further assumed that the intensity of radiation of any particular wave is proportional to the number of resonators which have got the requisite energy, *i.e.*,

$$E_\lambda = e^{-\frac{1}{2}mv^2/kT} \times \psi(v) = e^{-a\nu/kT} \times \psi(v),$$

where $\psi(v)$ is a function of the energy of the molecular resonator and hence of its velocity alone. It is therefore a function of the wavelength. We have, therefore, comparing with Wien's displacement law,

$$E_\lambda \, d\lambda = \frac{A}{\lambda^5} e^{-c_2/\lambda T} d\lambda. \qquad . \quad . \quad . \quad . \quad . \quad (41)$$

15·30. Comparison with Experimental Result.—Paschen working with short waves verified Wien's formula, but Lummer and Pringsheim, working with long waves and high temperatures, found considerable deviations from it. The value of c_2 is found to vary considerably with λ. This equation makes E vanish for $\lambda=0$ or $\lambda=\infty$ as it should do, but it makes E finite for $T=\infty$. Lord Rayleigh argued that it is unlikely that E should be finite for infinite values of T.

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[1] This formula must be carefully distinguished from Wien's Law.

[2] *Ann. d. Physik*, **58**, 662, 1896.

The radiation law of Lord Rayleigh is based upon two theorems, (1) the theorem of equipartition of energy, (2) the theorem of stationary waves in a hollow space. Jeans[1] and Lorentz showed later on that this was the only law consistent with the principles of classical dynamics. But it is quite evident that this law also cannot be true for, if we plot the spectral distribution of energy curve, it runs to infinity and gives no point of maximum emission. The total emission

$$\int E_\lambda \, d\lambda = 2ckT. \int_{\lambda_2}^{\lambda_1} \frac{d\lambda}{\lambda^4} = \tfrac{2}{3}\, ck.\, T \left[\frac{1}{\lambda_2{}^3} - \frac{1}{\lambda_1{}^3} \right],$$

where λ_1 and λ_2 are the upper and lower limits. As the upper limit we take infinity, then in order to make the expression finite, we have to assume that there is a limit to the shortness of the wave which can be emitted by a black body. The equation also shows that most of the energy is contained in the short waves. Now all these deductions are, as Rayleigh himself pointed out, against experimental evidence. In fact he remarked that the law could be expected to hold only in the case of emission of long waves. This was verified by Lummer and Kurlbaum who found that when λ was large, Rayleigh's law agreed with experimental results.

15·31. Planck's Law of Radiation.—The most satisfactory formula both on theoretical and experimental grounds is that of Planck which can be written as follows :—

$$u_\lambda \, d\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{1}{e^{hc/\lambda kT} - 1}. \quad \cdot \quad \cdot \quad \cdot \quad (42)$$

This equation agrees with the energy curves obtained by various investigators. We can readily show that both Wien's law as well as Rayleigh's law are simply particular cases of it.

Thus if λT is small, *Exp.* $(hc/\lambda kT) \gg 1$ and accordingly 1 in the denominator of (42) can be neglected. We get $u_\lambda = \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda k T}$ which is Wien's law.

If λT is large, *Exp* $(hc/\lambda kT)$ may be expanded by the exponential theorem, and we get $u_\lambda = (8\pi/\lambda^4)\, kT$ which is the Rayleigh-Jeans law.

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[1] *Phil. Mag.*, **10**, 91, 1905.

15·32. Deduction of Planck's Law.—There are various ways of deducing Planck's Law. If we start from the considerations given on p. 656 in which a chamber containing black radiation is considered to be full of photons in molecular chaos, the present problem simply reduces to the task of finding out the law of distribution of energy amongst the photons. The problem was attacked in this way in 1923 by S. N. Bose[1] (*vide* Bose-Einstein Statistics (Chap. XVII), but when Planck began his investigations, the quantum theory of radiation was unknown (in fact it was Planck's investigation on black radiation which gave rise to it) and in radiation problems the notion of temperature could be introduced only by considering the energy exchanges between matter and radiation. For this purpose Planck imagined that a black radiation chamber is filled up not only with radiation, but also with the molecules of a perfect gas. At that time, the exact mechanism of generation of light by atomic vibrations or of absorption of light by atoms and molecules was unknown and so radiation and gas molecules of the classical kinetic theory could not be assumed to exchange energy directly.[2] Planck therefore introduced resonators of molecular dimensions as the *via media* between radiation and gas molecules. These resonators absorb energy from the radiation, and transfer energy partly or wholly to the molecules when they collide with them. In this way thermodynamical equilibrium is established. The process is rather roundabout, but this was the only one possible at the time, and besides leading to the law of distribution of energy, it yielded other results of the highest importance in Physics.

The resonators introduced by Planck were dipole oscillators which may be described as Hertzian oscillators of molecular dimensions. He deduced that[3]

$$u_\nu = \frac{8\pi\nu^2}{c^3} E_\nu', \qquad . \quad . \quad . \quad . \quad . \quad (43)$$

whe u_ν denotes the density of ν-radiation and E_ν the mean energy of a resonator emitting ν-radiation.

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[1] *Zeits. f. Physik*, **26**, 178, 1924.

[2] Assuming the atoms to exchange energy with radiation by emission and absorption according to the laws of quantum theory, Einstein gave a proof of Planck's law in 1917 (see *Phys. Zeits.*, **18**, 121, 1917)

[2] For a proof of this see Note 10.

But according to classical ideas, $E_\nu = kT$, as the resonator collides frequently with the molecules, hence its energy is given by the law of equipartition. We have therefore

$$u_\nu = \frac{8\pi\nu^2}{c^3} kT, \quad . \quad . \quad . \quad . \quad . \quad (44)$$

which is again the Rayleigh-Jeans law.

As the procedure did not yield a formula consistent with experimental data, Planck abandoned the hypothesis of continuous emission of radiation by resonators, and assumed that they emit energy only when the energy absorbed is a certain minimum quantity ϵ or some *integral* multiple of ϵ. Thus a resonator which has an energy $(r+\theta)\epsilon$, (r=whole number, θ=a fraction) will remain quiescent until the energy absorbed amounts to $(r+1)\,\epsilon$ when the energy ϵ may be emitted and the resonator may revert back to the state with the energy $r\epsilon$. Thus radiation of energy ϵ can be obtained from resonators having the energy content ϵ, 2ϵ, $\ldots r\epsilon \ldots$ Let us now see what is the mean energy of these resonators.

This can be done by classsical methods, using Maxwell's formula[1], according to which the probability that a resonator will possess the energy E is *Exp.* $(-E/kT)$. Now let N_0, N_1, $N_2, \ldots N_r, \ldots.$ be the number of resonators having the energy,[2] $0, \epsilon$, 2ϵ, $\ldots. r\epsilon \ldots$ etc. Then we have

$$N = N_0+N_1 + N_2 + \ldots. N_r \quad \ldots..$$
$$E = \epsilon\,(N_1+2N_2 + 3N_3 + \ldots.).$$
$$N_r = N_0 \, Exp. \, (-r\epsilon/kT).$$

We obtain, by adding up, and putting $y = Exp. \, (-\epsilon/kT)$,

$$N = \frac{N_0}{1-y}; \;\; E = N_0 . \frac{y}{(1-y)^2}\epsilon.$$

Hence the mean energy of a resonator is

$$\frac{E}{N} = \frac{y\epsilon}{1-y} = \frac{\epsilon}{e^{\epsilon/kT}-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

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[1] This law of partitioning of energy was shown in Chap. IX to hold for any system of particles, oscillators etc. obeying classical statistics.

[2] According to wave-mechanics the possible energy values for a harmonic oscillator are $(n+\frac{1}{2})h\nu$ and not $nh\nu$ (see §16·11). For the average energy of the resonator we then get expression (45) together with an additional term $\frac{1}{2}h\nu$ which is called the null-point energy (see §16·12).

Thus we see that the mean energy[1] of the resonators is not kT, as given by the equipartition law but equal to $\frac{\epsilon}{e^{\epsilon/kT}-1}$ according to the quantum law.

Hence equation (43) for energy density inside the enclosure becomes

$$u_\nu\, d\nu = \frac{8\pi\nu^2}{c^3} \cdot \frac{\epsilon}{e^{\epsilon/kT}-1}\, d\nu. \quad . \quad . \quad . \quad . \quad (46)$$

Comparing with Wien's displacement law (32) we see that ϵ must be proportional to ν. Hence we write $\epsilon = h\nu$ where the constant of proportionality has been put equal to h. h is called the Planck's constant. We therefore obtain

$$u_\nu\, d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT}-1}\, d\nu; \quad . \quad . \quad . \quad . \quad (47)$$

or, since
$$d\nu = -\frac{c}{\lambda^2}\, d\lambda,$$

$$u_\lambda\, d\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{1}{e^{ch/\lambda kT}-1}\, d\lambda \quad (48)$$

which is Planck's law. This gives the energy-density for wavelength λ in the spectrum of a black body. The law has been verified by numerous experimenters. The experiments of Lummer and Pringsheim have already been described. For a more rigorous experimental test, see p. 673.

We have given a rough sketch of one of the ways in which the law of distribution of energy was arrived at by Planck. The method is not at all simple, is full of inner contradictions and contains assumptions, *e.g.*, discontinuity of emission in quanta of ϵ which were quite foreign to the ideas then prevalent. But contrary to expectations, the ideas came to stay and led by degrees to the most interesting developments in photo-electricity (Einstein 1906), to theories of spectral emission (Bohr 1913), and ultimately to the development of atom-mechanics as a whole.

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[1] We may multiply this mean energy by the number of waves $\frac{8\pi\nu^2}{c^3}\, d\nu$ (p. 666) per unit volume and thereby obtain the expression (46). The procedure is however not rigorous.

15·33. Further Deductions from Planck's Law.—Equation (42), which has been found by extensive experiments to be the correct law of distribution of energy in the spectrum of a black body contains only one new constant, *viz.*, h. From this equation it is possible to derive the other constants of the theory of radiation. This is done below.

(1) *Stefan's Constant* σ. From definition, we have

$$u = \int u_\nu \, d\nu = aT^4.$$

Taking the value of u_ν as obtained from (47), we have

$$aT^4 = \frac{8\pi h}{c^3}\int_0^\infty \frac{\nu^3 d\nu}{e^{h\nu/kT}-1} = \frac{8\pi k^4 T^4}{h^3c^3}\int_0^\infty \frac{x^3dx}{e^x-1},$$

where $x = h\nu/kT$. Hence we have

$$a = \frac{8\pi k^4}{h^3c^3}\int_0^\infty x^3dx\left(e^{-x}+e^{-2x}+\ldots e^{-rx}+\ldots\right) = \frac{48\pi k^4}{c^3h^3}\cdot\frac{\pi^4}{90},$$

because $$\int_0^\infty x^3e^{-rx}\,dx = \frac{6}{r^4}, \text{ and } \sum_{r=1}^{r=\infty}\frac{1}{r^4} = \frac{\pi^4}{90}.$$

Since $\sigma = ac/4$, we have

$$\sigma = \frac{2}{15}\frac{\pi^5k^4}{c^2h^3}. \qquad (48)$$

Wien's Constant b.—According to Wien's law (p. 660)

$$\lambda_m T = b,$$

where λ_m is the wavelength for which the emitted energy is maximum. λ_m is obtained from the equation $\partial E_\lambda/\partial\lambda = 0$.

Taking $E_\lambda = \frac{A}{\lambda^5}f(\lambda T)$, we find that this condition leads to the equation

$$\lambda_m T = 5\, f(\lambda T)/f'(\lambda T), \qquad (49)$$

where $$f' = \frac{\partial f}{\partial(\lambda T)}.$$

Now from Planck's law, $f(\lambda T) = \frac{1}{e^{c_2/\lambda T}-1}$, where $c_2 = ch/k$.

Put $\lambda_m T = x$. Then we find that (49) leads to the equation

$$\frac{c_2}{x} = 5\left(1 - e^{-c_2/x}\right). \qquad (50)$$

This is a transcendental equation, but it can be easily seen that x is very nearly equal to $c_2/5$. Actually $x = c_2/4 \cdot 9651$. Hence we have

$$\lambda_m T = b = \frac{ch}{k \times 4 \cdot 9651}. \qquad . \quad . \quad (51)$$

We shall now describe how the constant c_2 can be experimentally determined.

EXPERIMENTAL VERIFICATION OF PLANCK'S LAW.

15·34. We have already given a brief description of the experiments undertaken by Lummer and Pringsheim and by Paschen. After Planck had shown that the results of these experiments can be explained by his law, it became necessary to subject the formula to a more rigorous experimental test.

For this purpose, it is sufficient to show that the constant c_2 remains constant over all possible range of values of λ and of T. Assuming the validity of Planck's law, two important methods have been developed for finding out the value of c_2, and showing its constancy.

15·35. The Isothermal Method.—This is the same in principle as that used by Lummer and Pringsheim. The temperature of the furnace is kept constant and the intensity of radiation in different parts of the spectrum is measured. If absolute measurements be required, the thermopile or bolometer employed has to be calibrated in terms of radiant energy received. Corrections must also be made for the finite width of the slit and of the bolometer.

There are two ways of obtaining c_2 from the isothermal measurements. In the first, the isothermal spectral energy curve is drawn, from which the wavelength λ_m corresponding to the *maximum emission of energy* is noted. Then $c_2 = 4 \cdot 9651 \, \lambda_m T$, where T is the temperature at which the experiment is carried out. In actual practice it is found rather difficult to locate exactly the wave of maximum emission from the rounded top of the energy curve. Paschen therefore used a method, called the "*method of equal ordinates*" by means of which the constant c_2 can be calculated without finding out λ_m. A line is drawn parallel to the abscissa cutting the curve at the two points λ_1 and λ_2. We have, using Wien's equation,

$$E_1 = \frac{c_1}{\lambda_1^5} e^{-c_2/\lambda_1 T} = \frac{c_1}{\lambda_2^5} e^{-c_2/\lambda_2 T}$$

from which we obtain after some work

$$c_2 = 5T\frac{\lambda_1\lambda_2}{\lambda_2-\lambda_1}\Big[ln\,\lambda_2 - ln\,\lambda_1\Big]. \quad . \quad . \quad (52)$$

If however the range of the experiment be too wide for Wien's formula to hold good, Planck's law must be used. It can be proved from Planck's law that we have in this case

$$\frac{c_2}{T}\Big/\frac{\lambda_1\lambda_2}{\lambda_2-\lambda_1} = 5\,ln\frac{\lambda_2}{\lambda_1} - ln\left[\left(1-e^{-\frac{c_2}{\lambda_1 T}}\right)\Big/\left(1-e^{-\frac{c_2}{\lambda_2 T}}\right)\right]. \quad (53)$$

An approximate value of c_2 is substituted on the right-hand side and then the method of successive approximation is employed.

In Table 2 we reproduce the results of an experiment with the black body at the temperature 1442°K. The wavelengths λ_1, λ_2 having the same intensity of emission are given in the same vertical column, and the different vertical columns represent different pairs of wavelength having the same intensity. All the wavelengths are expressed in μ. It will be seen that the value of c_2 calculated from Planck's law is constant to about 5%.

Table 2.—Value of c_2 from the Isothermal Method.

λ_1 . . .	1·54	1·30	1·17	1·03	0·83
λ_2 . . .	2·74	3·45	4·03	4·95	7·22
c_2, Wien's law	14610	14650	14700	14720	14860
c_2, Planck's law	14510	14500	14490	14440	14390

15·36. The Isochromatic Method.—The isothermal method suffers from a serious disadvantage since the different regions of the spectrum are differently absorbed on their passage through the dispersing prism or through the lenses in the system. On this account the isochromatic method is sometimes preferred, especially when the absolute value of c_2 is required. As the name suggests, the emissions from a black body heated to different temperatures are compared for the same wavelength. Since the same wave is to pass through the prism, the emission at the two temperatures is absorbed in the same proportion, hence the ratio is unaffected. Rubens and Kurlbaum employed the residual rays from rocksalt (51·8μ), quartz (8·944μ) and fluorite (22·3μ). Writing out the equations from Planck's law we get

$$c_2\Big/\frac{\lambda T_1 T_2}{T_2-T_1} = ln\,\frac{E_2}{E_1} - ln\,\frac{1-Exp.\,(-c_2/\lambda T_1)}{1-Exp.\,(-c_2/\lambda T_2)}. \quad . \quad (54)$$

Warburg determined the value of the constant c_2 by using the method of isochromatics. A Lummer-Kurlbaum open radiator was heated to the temperature of 1337°K (melting point of gold) and 1575·2°K (melting point of nickel), and emissions at these temperatures were compared for the waves ($\lambda = 0 \cdot 6563\mu$, $1 \cdot 132\mu$, $1 \cdot 329\ \mu$, $1 \cdot 588\ \mu$, $2 \cdot 172\ \mu$) and c_2 was calculated from the formula (54). He produced the spectrum by means of a quartz prism.

Wensel[1] has given a full discussion of the values of radiation constants determined by different methods and adopts the value $c_2 = 1 \cdot 436$ cm. deg. For purposes of the international temperature scale the value of c_2 is taken to be 1·438 cm. deg. as the radiation constants can be determined more accurately from the values of the atomic constants [Vide equations (48) and (51)].

15·37. Experiments of Rubens and Michel.—About 1919 W. Nernst and Wulf pointed out that instead of the law (45), *viz.*,

$$E_\nu = h\nu/(e^x - 1),$$

where $x = h\nu/kT$ a law of the form

$$E_\nu = \frac{h\nu}{e^x - 1}(1 - \alpha), \quad . \quad . \quad . \quad . \quad (55)$$

where α is a small variable fraction, satisfies better the older experimental results. On account of the great importance of Planck's formula for modern developments in Physics, Rubens and Michel undertook a redetermination of the value of $c_2 = ch/k$ over a wide range of temperatures in order to find out whether Nernst and Wulf's hypothesis was correct. These experiments constitute the most thoroughgoing test of Planck's law and are described below :—

The experimental arrangement is shown in Fig. 21, p. 676. K stands for a blackbody radiator. Four different radiators were used :—(*i*) consisting of a copper cylinder with a narrow orifice, the inside being blackened by lampblack; this was used from liquid air temperature to room temperatures; (*ii*) from room temperatures to 550°C; this was also a copper cylinder with the inside blackened by copper oxide; (*iii*) from 550°C to 1400°C; it is identical with the one described on p. 634; (*iv*) from 1400°C to 1900°C ; it was of the same type as (*iii*), but the tube consisted of blackened magnesia. The radiation coming out of K passed through the water-cooled diaphragm D, of 1 cm. diameter, then fell upon the silvered plane mirror M_1 and from thence on the reflecting mirror H by which it was concentrated on the slit S_1 which could be closed by a diaphragm Q. The spectrometer was of the reflecting type used by Wadsworth. The prism used was of fluorite for $4\cdot5\mu$ to 7μ, rocksalt for 9μ to 12μ and sylvine for 12μ to 16μ. The concave mirrors H_1 and H_2 were of 5 cm. diameter and 35 cm. focal length. A small strip of the spectrum fell upon the second slit S_2, the radiation then fell upon the plane mirror M_2 from which it was reflected on to the concave mirror H_3 which formed an image of the slit S_2 on the thermo-element of the radio-micrometer T. The sensitiveness of the instrument was such that a Hefner lamp at a distance of 5 metres gave a deflection of 280 mm. on a scale placed at a distance of 5 metres and the null point remained constant to within 0·1 mm. The whole apparatus was enclosed in an airtight chamber. For short waves a window of rocksalt and for long waves a window of sylvine were used. Quartz window was used for measurement with rocksalt rays. For very long rays from 22μ to 52μ the method of residual rays[1] (Fig. 22) was used in which reflecting plates of fluorite or rocksalt were employed. For the first black body, temperatures were produced by suitable baths whose temperature was determined. For (*ii*) temperature was determined by a resistance pyrometer and for (*iii*) and (*iv*) by standardised Le Chatelier thermo-elements. The experiments

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[1] *Bull. Res. Bur. Stand.*, **22**, 375, 1939.

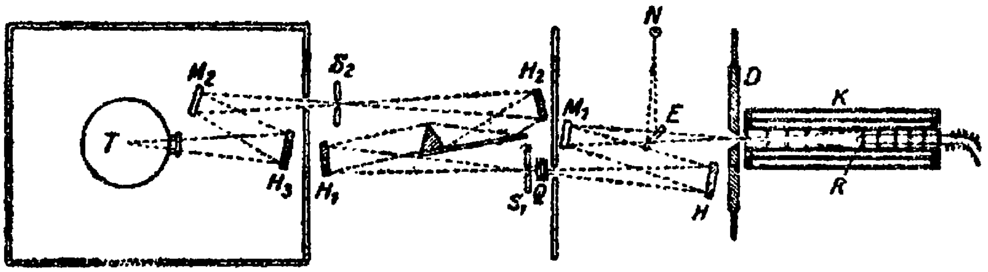

Fig. 21.—Experimental test of Planck's Law using a prism spectrometer.

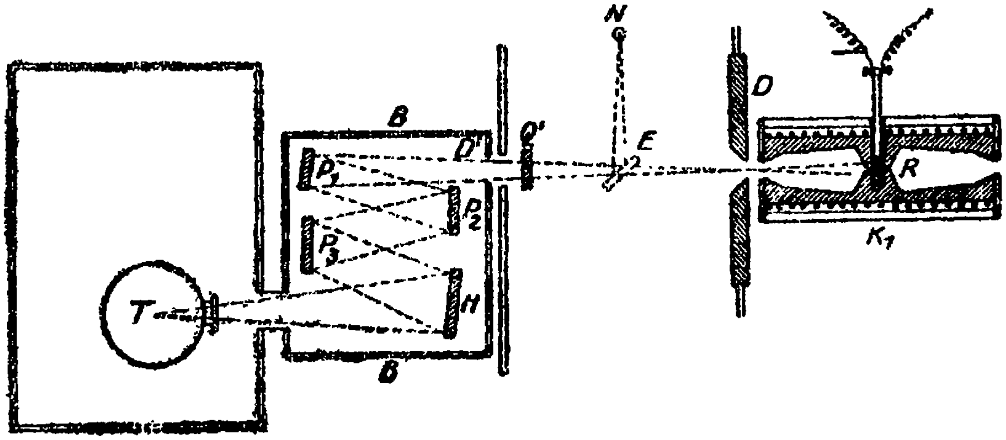

Fig. 22.—Method of Residual Rays.

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[1] For the method of residual rays, see Baly, *Spectroscopy*.

showed no deviation from Planck's law from liquid air temperature to 1831°K.

15·38. Radiation from Solid Bodies.—Up to this time, not much investigation has been carried out to find how emission from bodies other than black varies with temperature, except in the case of metallic filaments and a certain number of oxides. The problem can be solved if we proceed from Kirchhoff's law

$$e_\lambda = a_\lambda E_\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

and then find out an expression for a_λ in terms of T, and the physical properties of the substance. For metals, the electromagnetic theory of light enables us to calculate a_λ in terms of the specific electrical resistance ρ. It was shown by Drude that[1]

$$e_\lambda = 0\cdot365\left(\frac{\rho}{\lambda}\right)^{\frac{1}{2}} + 0\cdot0666\left(\frac{\rho}{\lambda}\right) + \dots \quad . \quad . \quad (57)$$

Equation (57) was found by Hagen and Rubens to hold good for long waves for a number of metals over a large temperature range. Now putting Planck's value of E_λ in (57) we have, as a first approximation,

$$e_\lambda = 0\cdot365\sqrt{\rho}\,\frac{2\pi c_1}{\lambda^{5+\frac{1}{2}}}\,\frac{1}{e^{c_2/\lambda T}-1}\,d\lambda, \quad . \quad . \quad . \quad . \quad (58)$$

and the total radiation

$$e = \int e_\lambda\,d\lambda = \frac{2\pi c_1}{c_2^{4.5}}\,\Gamma(4\cdot5)\times0\cdot365\,\rho^{\frac{1}{2}}\,T^{4.5} \quad . \quad . \quad (59)$$

i.e., if ρ be supposed to be constant, the total emission should vary as $T^{4.5}$. Let e_e denote the emission coefficient, *i.e.*, the ratio of emissivity of the metal to that of the black body. Then

$$e_e = 0\cdot365\,\frac{\Gamma(4\cdot5)}{\Gamma(4)}\,\frac{\sqrt{\rho T}}{c_2}\;0\cdot576(\rho T)^{\frac{1}{2}}. \quad . \quad . \quad (60)$$

where $\Gamma(n)$ denotes a gamma function.

If on the other hand, we suppose that the resistance varies as absolute temperature, *i.e.*, $\rho = \rho_0 T/273$, we find that

$$e_e = 0\cdot0349\,\rho_0^{\frac{1}{2}}/T. \quad . \quad . \quad . \quad . \quad (61)$$

Equation (60) should hold for substances like constantan which have a small temperature coefficient of resistance and (61) for pure metals like platinum.

It can also be easily verified that

$$\lambda_m T = \text{const.}$$

but this constant is generally less than the Wien's constant $b=0\cdot288$. For Pt it is found to be 0·263.

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[1] *Vide* Drude, *Physik des Aethers.*

The value of e_0 in the case of metals steadily rises with temperature. Davisson and Weeks investigated the emission from Pt between 300°K to 1000°K, and found that e_0 varies from 0·0359 to 0·192. For tungsten, which can be heated to a temperature of 3500°K, e_0 rises from 0·10 at 1000° to 0·40 at 3500°. The oxides are found to be much better radiators. The emission coefficient of oxidised steel amounts to as much as 0·787 at 873°K.

It is however more instructive to measure the spectral emission coefficient *i.e.*, the ratio e_λ/E_λ rather than the total emission coefficient. The data[1] for tungsten, the most thoroughly investigated substance, are as follows:—At $\lambda > 2{\cdot}5\mu$ the values for the emission coefficient as well as its variation with λ and T are closely given by Drude's relation (58) but for $\lambda < 2{\cdot}5\mu$ this relation totally fails. At $\lambda > 1{\cdot}27\mu$ the emission coefficient increases with increase in T but below $\lambda = 1{\cdot}27\mu$ it decreases while at $\lambda = 1{\cdot}27\mu$ it does not vary at all. At a fixed temperature the emission coefficient varies with the wavelength. Thus for tungsten at 2450°K the emission coefficient is 0·47 at $0{\cdot}5\mu$, 0·40 at $1{\cdot}0\mu$, and 0·26 at $2{\cdot}0\mu$. Further the wavelength λ_m for maximum emission is $1{\cdot}160\mu$ while for the blackbody at the same temperature it is $1{\cdot}182\mu$.

The foregoing characteristics of a non-blackbody enable us to define a 'colour temperature' T_c for most non-blackbodies. The colour temperature T_c for a non-blackbody at the temperature T is that temperature at which if a blackbody were maintained, it would emit radiations of such intensity that the ratio $e_{\lambda, T}/E_{\lambda, T_c}$ (*i.e.*, ratio of spectral emission from non-blackbody at $T°$ to emission from blackbody at the temperature T_c) is constant for the visible and near infra-red regions. It is obvious that under these conditions a match in colour between the black and the non-black sources will be obtained. The colour temperature of tungsten at 2450°K is 2500°K the emission ratio being constant at about 0·358 in the required region. The colour temperatures of most incandescent metals is found to be greater than their true temperatures, but the difference is generally very small. Hence the temperature of substances is often measured with the help of colour-match pyrometers in which the colour of the incandescent source is matched with the colour of the light from a calibrated tungsten lamp.

For detailed information, the report by H. Schmidt in the *Ergebnisse der exakten Naturwissenschaften*, Vol. 7. p. 342, or *Heat* by Worthing and Halliday (1948), Chap. XIII, published by John Wiley and Sons, may be consulted.

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[1] For data on emissivity etc., see McAdams, *Heat Transmission*, McGraw-Hill Book Co.

RADIOMETERS[1]

We shall now describe a few instruments which are used for the measurement of radiation.

15·39. Thermo-elements.—The principle of these instruments has been already described. In radiation measurements, we have sometimes to deal with very minute amounts of energy (*e.g.*, radiation from stars) and hence the apparatus must be extremely sensitive. In the design of thermopiles, the following considerations have to be borne in mind :—(1) metals used should give large thermo-E.M.F.; (2) junctions should be as thin as possible; (3) connecting wires should be thin so as to minimise the loss of heat by conduction; (4) hot junction should be coated with lampblack so that all the heat falling on it may be absorbed; (5) it should be mounted in vacuum, so that there is no loss of heat by convection, and the deflections remain steady.

These conditions are fulfilled in a thermopile designed by W. W. Coblentz[2] which was used for measurement of radiation from the planet Mars. The thermopiles consisted of:

1.	60 Au 40 Pd	1	(Sensitiveness)
2.	90 Pt 10 Rh	2·85	,,
3.	95 Bi 5 Sn	3·65	,,
4.	97 Bi 3 Sb	5·35	,,

Strips were 0·02 to 0·025 mm. thick. The other arm was of silver.

The elements were enclosed in a glass globe provided with rock-salt window. By mounting in vacuum, the sensitiveness was increased only by 50 to 100%, but the null point remained perfectly steady.

The galvanometers should be of low resistance type with high voltage sensitiveness. It is not unusual to be called upon to measure voltages which are as small as 10^{-4} volts. The galvanometers usually employed are the Broca, the Paschen, and sometimes Thompson galvanometers. These are all of the suspended magnet (astatic) type, and are therefore very much susceptible to external magnetic disturbances. They have been successfully used only by very skilled observers.

The suspended coil type galvanometers are not generally found to be sufficiently sensitive on account of their high resistance. Moll and Burger[1] have however devised a method of magnifying deflections of coil galvanometers by a relay arrangement and this has been used for radiation measurements.

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[1] For various other instruments now used for measuring radiant energy see *Measurement of Radiant Energy* by W. E. Forsythe, published by McGraw-Hill Book Co. (1937).

[2] *Bull. Bur. of Standards*, **9**, 7, 1913; **11**, 131, 613, 1915; **17**, 725, 1922.

The apparatus is shown in Fig. 23. AB and CD are thin foils of constantan 0·5 mm. broad, BC is a similar manganin strip. The foils are mounted in a glass vessel, which is perfectly evacuated. If now a thin line of light falls at the middle point of the manganin strip, no thermo-current is produced. If however the thin line of light is shifted on one side, the two junctions are unequally heated, and a thermo E. M. F. is generated. This can be measured by a highly sensitive coil galvanometer of low resistance.

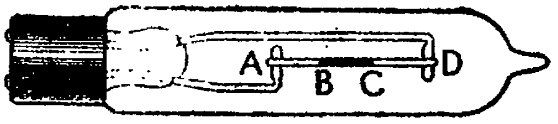

Fig. 23.—Moll and Burger's galvanometer relay.

In actual practice, radiation is allowed to fall on a vacuum thermopile. This is directly connected to a Moll galvanometer. This galvanometer is so constructed that it has practically no lag, and has its zero-point absolutely steady. Light from a single filament four-volt lamp is allowed to fall on the galvanometer mirror, and is then focussed by means of a cylindrical lens on the thermo-element ABCD, which is then connected through the highly sensitive second galvanometer. In this way a magnification of about 300 has been secured.

15·40. The Bolometer.—The bolometer is now much less used, being superseded by modern types of thermopile. It was invented by S. P. Langley[2] and depends for its action on the change of resistance of platinum wires when heated.

The sensitiveness of the bolometer depends (1) on the sensitiveness of the galvanometer; (2) on the thinness of the strips, because the thinner the strips the larger will be the rise in temperature and the increase in resistance for a given amount of incident radiation.

Two types of bolometers have been used in radiation measurements: (1) the surface bolometer for total radiation measurements; (2) the linear bolometer for measurement of distribution of energy in the spectrum of the black body.

The surface bolometer consists of exceedingly thin strips of platinum, 1 to 2×10^{-3} mm. thick joined together in series. The method of constructing such a thin conductor is as follows :—A sheet of platinum is welded to a thick sheet of silver and the composite sheet is rolled. The sheet is then punched out as shown in Fig. 24, and attached to a hollow frame of slate. The silver is then dissolved off in nitric acid, the end joints being protected by a coating of varnish. The strips are then coated with platinum black. Fig. 25 shows a front view of such grid. A grid so constructed has a resistance of about 60 ohms.

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[1] *Zeits. f. Physik*, **32**, 575, 1925.

[2] *Proc. Amer. Acad. Arts and Sciences*, **16**, 342, 1881.

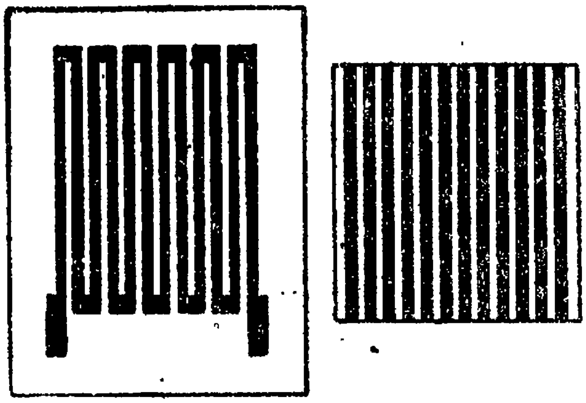

Fig. 24 and 25.—The surface Bolometer.

For experimental purposes four such grids, similar in all respects to each other, are connected in the form of a wheatstone bridge. The method of connecting the grids is shown in Fig. 26. The grids 1 and 3 are in opposite arms of the wheatstone bridge and are so arranged that the strips in (3) receive the radiation passing between the strips in (1) and so the effect is doubled; 2 and 4 are similarly arranged but are protected from radiation. The whole is enclosed in a box. In the absence of incident radiation the galvanometer shows no deflection. When radiation is incident on grids 1 and 3 a deflection is produced.

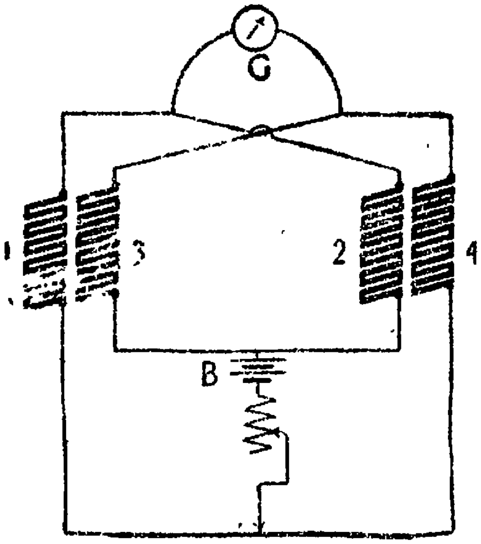

Fig. 26.—Connections of the Bolometer.

In the linear bolometer a single narrow and thin strip of platinum is used and one such strip is arranged in each of the two arms of the Wheat stone's bridge. Many improvements have been made by Abbot in the construction of the bolometer as a result of which it has become a very suitable instrument for use. By placing the bolometer strips inside a glass enclosure which is evacuated to less than 0·001 mm. pressure the sensitiveness is increased ten times. Such a vacuum bolometer has been much used by the Smithsonian Astrophysical Observatory.

15·41. The Radiomicrometer.—This was invented by C. V. Boys and is essentially a thermocouple without an external galvanometer. A single loop *c* of fine copper or silver wire is suspended (Fig. 27) between the poles of a strong permanent magnet NS as in a suspended coil galvanometer. To the lower ends of the copper wire two thin bars of antimony Sb and bismuth Bi are attached, and the lower ends of these are again attached to a thin disc *d* or narrow strip of blackened copper. To the upper end of the copper loop is attached a thin glass rod *g* carrying a light galvanometer mirror *m* for measuring deflection, the glass rod itself being attached to a fine quartz suspension *q*. The whole system is extremely light. Radiation, falling horizontally on the copper disc, heats the junction of antimony and bismuth and an electric current flows through the copper coil causing a deflection which depends upon the intensity of the energy received by the copper disc. To prevent disturbances due to diamagnetism of bismuth, the rods of the thermocouple are surrounded by a mass of soft iron I. The whole suspended system is enclosed in brass (shown shaded in the diagram).

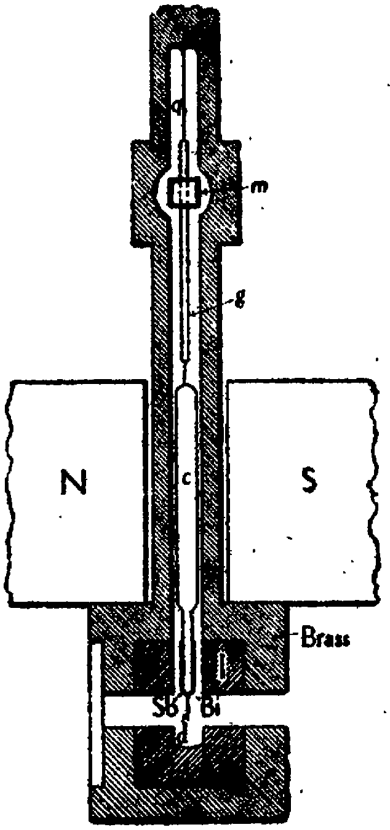

Fig. 27.—Boys' Radiomicrometer[1].

Radiometer.—The well-known early form of radiometer given by Crookes was described in §3·62 and its action was briefly discussed there. This form of the instrument is however not suitable for exact measurements of radiation. An accurate instrument of this type however can be made by attaching two equally big wings of mica or aluminium to a thin quartz fibre carrying a mirror. The quartz fibre is suspended as in a galvanometer and one of the wings is blackened. When radiation falls on the instrument, it rotates. Accurate instruments of this type were developed by Rubens and Nichols, Brüche and Littwin[2] and others, and a theory of the radiometer action was given by Hettner[3].

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[1] Reproduced from 'The Theory of Heat' by Preston by the kind permission of Messrs. Macmillan & Co.

[2] *Zeits. f. Phys.*, **67**, 333, 1931.

[3] See *Ergebnisse d. exakten Naturwiss.*, **7**, 209, 1928.

RADIATION PYROMETRY

15·42. Temperature from Radiation Measurement.—In the foregoing pages we have seen that the radiation emitted by a black body depends upon its temperature and upon nothing else. Hence if we measure the radiation emitted by the body with the help of some instrument we can find its temperature. We may either measure the total radiation emitted by the body and deduce the temperature by making use of Stefan's Law ($T \propto E^{\frac{1}{4}}$). These are called 'Total Radiation Pyrometers.' Or we may measure the energy emitted in a particular portion of the spectrum $E_\lambda \, d\lambda$ and make use of Planck's law of distribution of energy in the spectrum. These are called Spectral or Optical Pyrometers.

Radiation pyrometers possess the great advantage that they can be employed to measure any temperature however high that may be or wherever the object may be. The pyrometer itself has not to be raised to that temperature nor need it be placed in contact with the hot body. Further there is no extrapolation difficulty as the radiation formulæ have been found to hold rigorously for all temperatures. But the radiation pyrometer suffers from a serious drawback. It can measure accurately the temperature of black bodies only.

It is however generally employed to measure the temperature of any hot source. In that case it gives that temperature at which a perfectly black body would have the same intensity of emission (total or spectral) as the body whose temperature is being measured. This temperature is called the 'Black Body Temperature' of the substance, and is consequently lower in all cases than its actual temperature. The greater the departure from perfect blackness, the greater is the error involved. The lower practical limit for radiation pyrometers is about 600°C for then the emission for the body becomes too small to be measured accurately. Recently, however, Strong[1] has developed an infra-red spectral pyrometer which can be used to measure temperatures even lower than the room temperature.

15·43. Total Radiation Pyrometers.—Féry was the first to devise a radiation pyrometer based on Stefan's law. These pyrometers are merely thermopiles so arranged that the readings are independent of the distance between the hot body and the pyrometer. We shall describe Féry mirror pyrometer which is typical of this class. Fig. 28 shows a modern type of the instrument. Radiation, incident in the direction of the arrows, falls on the concave mirror *M* which can be moved backwards and forwards for the purpose of focussing the radiation on the receiver S, to which the hot junction of the thermocouple is attached. The cold junction of the thermocouple is protected from radiation by the tongue T and is further surrounded by the box B, which also contains the thermocouple receiver and is provided with a small opening just in front of S. The electromotive force developed is read on a millivoltmeter connected as indicated in Fig. 29. The instrument possesses no lag, the steady state being reached in about a minute.

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[1] *J. Opt. Soc. Am.*, **29**, 520, 1939.

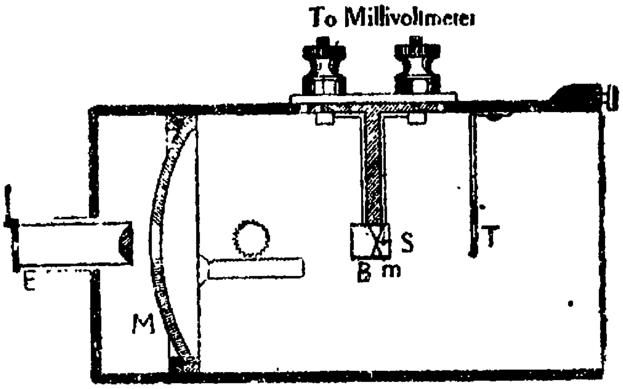

Fig. 28.—Féry Radiation Pyrometer.

To enable the observer to focus the radiation accurately on the thermocouple, Féry employs two semicircular mirrors (Fig. 29) inclined to each other at an angle of about 5° and placed immediately in front of S, an opening of about 1·5 mm. being left at the centre of the mirror to allow the incident radiation to pass. Now if the image of a straight line formed by the concave mirror does not lie in the plane of the inclined mirrors, these latter will form two images separated by a distance (see Fig. 29) and the line will appear broken when seen through the eyepiece E. The concave mirror is moved till this relative displacement of the two halves of the image disappears, and then the apparatus becomes adjusted. It will be easily seen that so long as the heat image formed by the concave mirror is larger than the hole, the thermocouple measures the intensity of the heat image and not the total radiation. For if the distance of the object is doubled, the amount of radiation falling on the mirror is reduced to one-fourth, but as the area of the image is also simultaneously reduced to one-fourth the intensity is unaltered. Thus the indications of the instrument are independent of the distance. Hence in actual use it is essential that the object, whose temperature is to be measured, should be sufficiently large and should be placed at not very great distance in order that its image is always bigger than the aperture in the box which in ordinary instruments is about 1·5 mm. diameter.

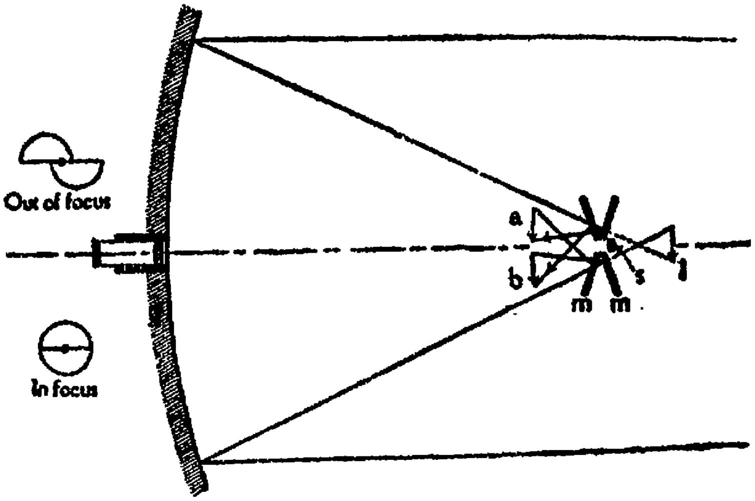

Fig. 29.—Focussing device.

The E.M.F. of the couple in these cases is given by the relation

$$E = a(T^b - T_0^b), \quad . \quad . \quad . \quad . \quad (62)$$

where T is the temperature of the black body, T_0 the temperature of the receiver S, 'b' a constant which varies from 3·8 to 4·2, depending upon the instrument and a depends upon the Stefan's constant, the reflecting power of the mirror, the absorptive power of the thermo-junction etc. Generally T_0 can be neglected in comparison with T and b may be put equal to 4. The departure from the index value of 4 is due to various causes :—

(1) E.M.F. generated is not exactly proportional to the difference of temperature between the two junctions.

(2) Stray reflections cause error.

(3) Conduction along the leads raises the temperature of the cold junction to some extent.

(4) The heat loss from the hot junction is not proportional to the temperature excess.

It is for these reasons that the pyrometer has to be calibrated by actual comparison with a standard thermometer, using radiation from a blackbody chamber or a heated strip. For high temperatures a rotating sectored disc is employed to allow only a fraction of the incident radiation to enter the pyrometer. If the sector[1] makes an angle θ at the centre, the fraction of energy passing is $(2\pi - \theta)/2\pi$. Hence if T is the true temperature of a blackbody, T_1 the temperature indicated by a pyrometer with the sectored disc, we should have

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[1] See Mendenhall and Forsythe, *Phys. Rev.*, 4, 69, 1914.

$$k_1 T_1^4 = k_1 \frac{2\pi-\theta}{2\pi} T^4,$$

whence T can be found.

The pyrometer so calibrated will correctly measure the temperature of black bodies only. Generally however it is often used to measure the temperature of non-blackbodies also when corrections must be applied to get the true temperature.

For the purpose of calibration let the pyrometer be sighted on a black body at the temperature T_1 and d_1 be the deflection produced in the galvanometer. Then

$$d_1 = k_1(T_1^4 - T_0^4), \quad . \quad . \quad . \quad . \quad (63)$$

where T_0 is the temperature of the pyrometer surroundings. Now if the pyrometer is sighted on a non-blackbody at the temperature T_2 having an emission coefficient e_e and reflectivity r' for radiations from the pyrometer surroundings at the temperature T_0, then the deflection d_2 in the galvanometer is given by the relation

$$d_2 = k_1 \left(e_e T_2^4 + r' T_0^4 - T_0^4\right). \quad . \quad . \quad . \quad (64)$$

Equation (64) with the help of (63) yields

$$e_e T_2^4 = \frac{d_2}{d_1}(T_1^4 - T_0^4) + T_0^4(1-r') = T_B^4. \quad . \quad (65)$$

where T_B is called the blackbody temperature of the source. e_e is determined experimentally by sighting on the body at the temperature T_2 and then on a blackbody at the same temperature. If the respective deflections are d_3 and d_4 we have

$$\frac{d_3}{d_4} = \frac{e_e T_2^4 + r' T_0^4 - T_0^4}{T_2^4 - T_0^4}. \quad . \quad . \quad . \quad (66)$$

Roughly[1] we may assume $r' = 1 - e_e$. Then (66) yields $e_e = d_3/d_4$. This value of e_e is substituted in (65) and r' in (65) may be assumed to be equal to $1 - e_e$; then (65) gives us the required T_2.

15·44. Optical Pyrometers.—In these, the intensity of radiation from a blackbody in a small width of the spectrum lying between λ and $\lambda + d\lambda$ is compared with the intensity of emission of the same colour from a standard lamp. The formulæ required for this case can be easily worked out by assuming Wien's law.[2]

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[1] Rigorously speaking $e_e = 1 - r$ where r is the reflectivity for black radiation at T_2 but the difference between r and r' is generally small.

[2] In these experiments $e^{c_1/\lambda T} \gg 1$ and hence Planck's law reduces to Wien's law.

If E_1 denotes the intensity of emission for the wavelength λ of a blackbody at temperature T_1, and E_2 the intensity of the comparison lamp at the temperature T_2, we have (assuming Wien's Law)

$$E_1 = \frac{C_1}{\lambda^5} e^{-c_2/\lambda T_1}, \quad E_2 = \frac{C_1}{\lambda^5} e^{-c_2/\lambda T_2}$$

Hence[1]

$$ln \frac{E_1}{E_2} = \frac{c_2}{\lambda} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad . \quad . \quad . \quad . \quad (67)$$

The two well-known methods of comparing the intensity are the following :—

(1) The standard light is varied until it is equal to the intensity of the source. The thermometers based on this method are called pyrometers of the *Disappearing Filament type.*

(2) The standard light is maintained constant and the intensity of the light from the source varied in the instrument until it is equal to that of the standard. This is also called the *Polarising type.* We now proceed to describe these two important types of instruments.

15·45. The Disappearing Filament Pyrometer.—This type of pyrometer was first introduced by Morse in America. It was later improved by Holborn and Kurlbaum, and by Mendenhall and Forsythe. A pyrometer of this type is shown in Fig. 30. It is essentially a telescope having a lamp at the position usually occupied by the cross-wires. C is a metal tube containing the filament of a lamp L which is heated by the battery B and the current can be adjusted to any amount by varying the rheostat R. Radiation from the source whose temperature is required is focussed by the lens D on the lamp L where a heat image is formed. The lamp is viewed through the eyepiece E in front of which is placed a red filter glass. Besides, there are a number of limiting diaphragms.

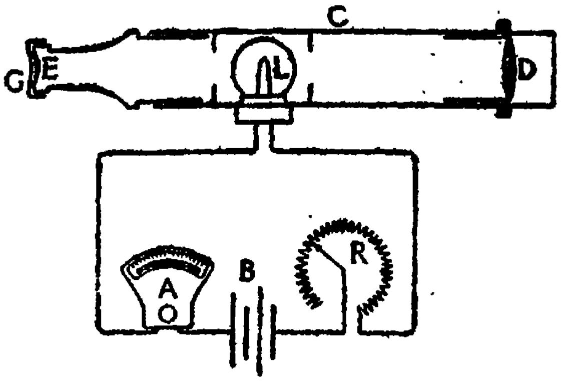

Fig. 30.—Disappearing Filament type Pyrometer

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[1] If the substance whose temperature is required is a non-black-body, its spectral emission coefficient must be known or determined previously.

In actual practice the observer looks through E and varies the current in the lamp till the filament becomes invisible against the image of the source. If the current is too strong the filament stands out brightly, while if the current is too weak the filament looks black. The filter glass enables this matching to be done for approximately monochromatic radiation. The instrument is calibrated by direct comparison with a standard thermocouple and then extrapolated by the use of rotating sectors. Thus from the strength of the current required to match the radiation, the temperature of the incident radiation can be deduced. Sometimes the ammeter is directly calibrated in degrees.

A disappearing-spot pyrometer has also been designed which works on exactly the same principle.

15·46. Henning's Spectral Pyrometer.—Difficulties which occur by our uncertain definition of λ are avoided in the spectral pyrometer of Henning. In this instrument the light before reaching the eye is decomposed by a prism so that matching is done for a very short interval $d\lambda$. In other respects it is similar to the pyrometer of Holborn and Kurlbaum. It has the advantage that it gives a clear picture of the object, but on account of spectral decomposition it has less light gathering power and cannot be used below 1000°C.

The part of the spectral pyrometer (Fig. 31) facing the radiator with the objective and occular lenses L_4 and L_3 as well as the glow lamp G has the same arrangement as in Holborn and Kurlbaum's apparatus. At R we can introduce smoked glasses in the path of the ray. The

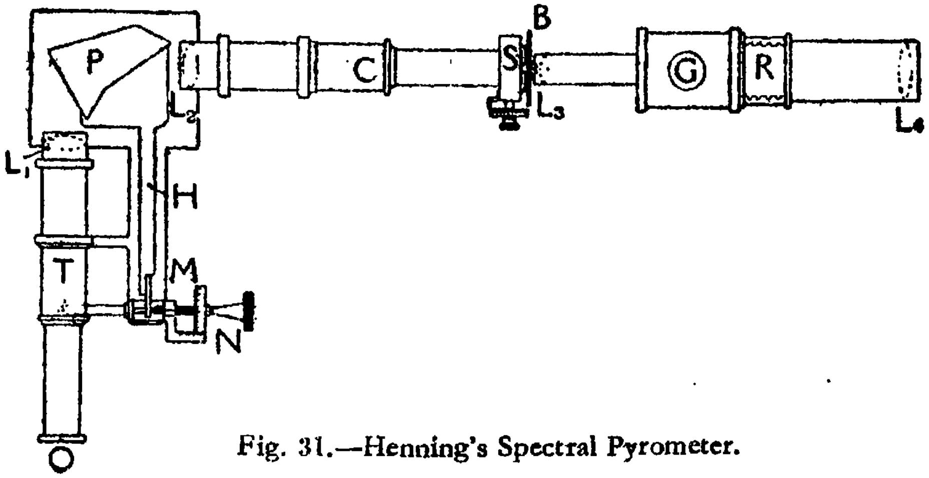

Fig. 31.—Henning's Spectral Pyrometer.

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[1] A combination of glass filters has also been used. See Egerton and Milford, *Proc. Roy. Soc.*, **130**, 111, 1931; Cunnold, *ibid*, **152**, 64, 1935.

light enters through the slit S behind L_3 into the collimator tube C, is dispersed by the totally reflecting Abbe prism P which can be rotated by the micrometer screw MN and the lever arm H. The telescope T is provided with the occular slit O. If it is properly adjusted a normal eye will see clearly the radiator as well as the filament of the glow lamp, in fact both in the same definite spectral colour, the purity of which depends upon the breadth of the slit S. The instrument is calibrated by actual comparison with thermocouple. Experiments have shown that keeping a wavelength λ fixed, the temperature T of the blackbody can be represented as a function of the current strength, and hence the temperature can be found from the reading in the ammeter. For fuller description, see Henning, *Temperaturmessung*.

A similar apparatus fitted with a spectroscopic eyepiece has also been devised by Mendenhall.

15·47. Strong's Infra-red Spectral Pyrometer.— This utilises the residual rays from quartz whose narrow band is located at $8 \cdot 8\mu$. The radiation from the source whose temperature is to be measured, suffers successive reflections from a number of quartz mirrors and is focussed by concave mirrors on to a thermocouple junction. The calibration has to be done as with the other spectral pyrometers. Visible and near infra-red radiations do not affect this $8 \cdot 8\mu$ pyrometer; further glass is opaque to this particular radiation. The pyrometer can be used to measure the temperature of bodies above and below the room temperature.

15·48. Polarising Pyrometer.—In 1901, Wanner constructed another pyrometer in which the comparison was made with the aid of a polarising device. Here the ray of a particular colour from the source is compared with a ray of the same colour obtained from a standard electric lamp. A diagram illustrating the essential parts of the instrument is given in Fig. 32. *a*, *b* are two circular holes arranged symmetri-

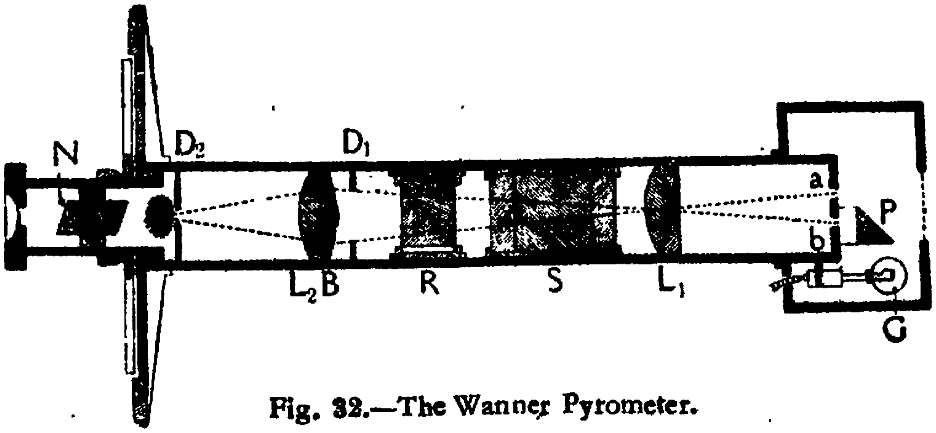

Fig. 32.—The Wanner Pyrometer.

cally about the optical axis of the system. Radiation from the hot source enters the system through *a* while the comparison beam is supplied by the electric lamp G which illuminates the right-angled prism P, and the latter directs the light on to *b*. Both beams are rendered parallel by means of an achromatic lens L_1, which is placed at a distance from the slit equal to its focal length. The parallel beams are dispersed by the direct vision spectroscope S and then pass through the polarising Rochon prism R which separates each beam into two beams polarised in orthogonal planes. B is a biprism placed in contact with a second achromatic lens L_2 which focusses the two beams on the slit D_2. The biprism produces in the two beams deviations of such amount that one image from each source is brought into juxtaposition. Since the holes *a*, *b* are at the focus of the lens L_1, the images produced by the second lens are also circular but the biprism splits them into semicircles. Six out of the eight images are stopped out while the remaining two are observed through the nicol N.

If the two beams are of equal intensity a uniformly illuminated disc with a diametrical line is observed if the plane of polarisation of the nicol prism makes an angle of 45° with the plane of polarisation of each component. Rotating the nicol in either direction diminishes the brightness of one image and augments that of the other. If the two beams are of unequal intensity, matching is effected by rotating the nicol prism in either direction. A graduated circle is attached to the analyser to observe the angle of rotation ϕ. The theory of the instrument is as follows :—

It can be easily shown with the help of the law of Malus regarding the amplitude of the polarised component of a light wave, that if E_1 and E_2 are the intensities of two plane-polarised beams matching a constant source at angles ϕ_1, ϕ_2, then

$$\frac{E_1}{E_2} = \frac{\tan^2\phi_1}{\tan^2\phi_2}.$$

Now if E_1 be the intensity of wavelength λ at temperature T_1 while E_2 is the intensity at temperature T_2 for the same wavelength, we have by Wien's law as on p. 687,

$$ln\,\frac{E_1}{E_2} = \frac{c_2}{\lambda}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = ln\,\frac{\tan^2\phi_1}{\tan^2\phi_2}$$

$$\therefore\ 2\,(ln \tan\phi_1 - ln \tan\phi_2) = \frac{c_2}{\lambda}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

It is thus seen that the relation between ϕ and T is of the form

$$ln \tan\phi = a + \frac{b}{T}. \qquad \ldots\ldots \qquad (68)$$

If we determine two values of ϕ corresponding to two values of T we get a straight line from which the temperature for any value of ϕ can be read. In practice the pyrometer is calibrated by direct comparison with a standard thermometer, and the disc is directly graduated in degrees.

15·49. Colour Match Pyrometers.—The principle of colour match pyrometry has already been discussed in §15·38. In this the temperature of a blackbody is so adjusted that its spectral brightness distribution (*i.e.* colour) in the visible and near infra-red regions is the same as that of a source whose temperature is required. The temperature of the blackbody satisfying this condition is called the colour temperature T_c of the source. The comparison is done with the help of a spectrophotometer and various instruments[1] have been devised to effect this comparison. The utility of the method lies in the fact that the colour temperature is only slightly different from the true temperature of the body. Thus for tungsten at 2450°K, the colour temperature is 2504°K while the temperature as determined by a spectral brightness pyrometer is 2233°K.

RADIATION FROM THE SUN

15·50. The Solar Constant.—The sun emits radiant energy continuously in space of which an insignificant part reaches the earth. But even of this incoming radiation, a considerable portion is lost by reflection and scattering by the terrestrial atmosphere and is sent back to the interstellar space. The best reflecting constituents of the atmosphere are water, snow and cloud. The scattering is partly due to the dust particles and partly due to the air molecules and is generally small. Further, the radiation is heavily absorbed by the earth's atmosphere, the total absorption varying from 20 to 40 % depending upon the time of the day and the season of the year. We naturally seek for a more constant quantity which is furnished by the rate at which solar radiations are received by one sq. cm. of black surface held at right angles to the sun's rays and placed at the mean distance of the earth, provided there were no absorption in the atmosphere or provided the atmosphere were not present. This is called the *solar constant* and is generally expressed in calories per minute. We shall now describe a method of determining the solar constant.

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[1] For detailed description the reader may consult *Heat* by Worthing and Halliday, Chap. XIII.

15·51. Determination of the Solar Constant.—Among the early workers who attempted to measure the solar constant were Pouillet, Langley and Wilson. The instruments employed for measuring solar radiation are called pyrheliometers or actinometers. They are of two types :—

(1) The absolute pyrheliometer in which the energy is measured directly. (2) Secondary pyrheliometers, which have been previously calibrated by comparison with an absolute pyrheliometer. The various methods employed make use of calorimetric arrangements, a pyrheliometer, a bolometer, a thermo-electric couple, a photographic paper, a black-bulb thermometer, chemical decomposition and so forth.

We shall here describe only two of these—(1) the absolute pyrheliometer, (2) the 'compensation pyrheliometer' of Ångström.

The *Water-Stir Pyrheliometer* employed in the Astrophysical Observatory of the Smithsonian Institution, Washington, U. S. A., is an absolute pyrheliometer as with its help the energy can be measured in ergs. Fig. 33 gives a cross-sectional view of the apparatus. AA is the black body chamber for the reception of solar radiation which is further protected from air currents by a vestibule, not shown. This is simply a hollow cylinder placed in front of AA. The chamber is blackened inside and has its rear end of conical shape, and is surrounded by water contained in the calorimeter DD which is stirred vigorously

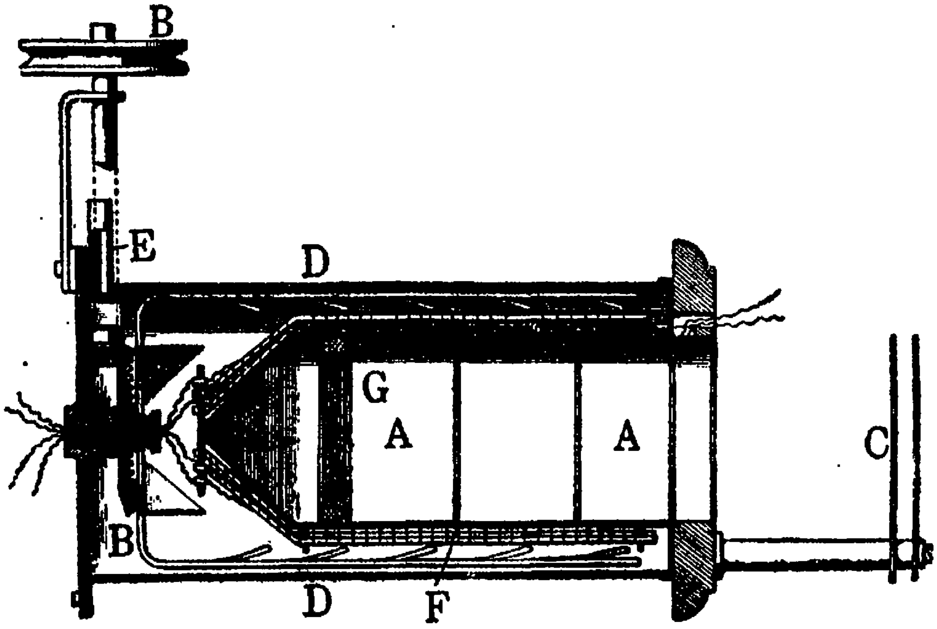

Fig. 33.—The Water-stir Pyrheliometer.

by means of a stirring arrangement BB run by an electric motor from outside. C is a diaphragm of known aperture for admitting the solar radiation. The incident radiation is completely absorbed by the chamber producing a rise in temperature of the water contained in the calorimeter. This rise is measured by the platinum resistance thermometer F whose wire is carefully wound upon an insulating frame round AA. At E is inserted a mercury thermometer. The calorimeter DD is carefully insulated from thermal effects occurring outside.

For calibrating the instrument, a known amount of electrical energy is supplied to the manganin resistance wire G and the rise in temperature noted. Thus the heat obtained by solar radiation can be compared with the heat generated electrically.

Another type of pyrheliometer is called the *Water-Flow Pyrheliometer*. In this a steady stream of water flows past the absorption chamber and the temperature difference between the incoming and outgoing water is observed.

In the 'compensation pyrheliometer' of Ångström there are two thin strips of metal identical in every way which serve as the calorimetric body. One of these is exposed to the sun while through the other, which is kept in shade, an electric current is passed. The strength of the current is so regulated that the temperatures of the two strips, as indicated by thermocouples attached in opposition, is the same. The energy of the incident radiation is then equal to the electrical energy supplied. If the breadth of the strips is b, their absorption coefficient a and the incident radiation equal to H per cm^2 per minute, then the radiant energy received per unit length of the strips is Hab calories. Again if r is the resistance per unit length and i the required current, the electrical energy$=i^2r\times 60/4{\cdot}18$ cal. Equating we get

$$H=\frac{60}{4{\cdot}18}\cdot\frac{i^2r}{ab}\text{ cal. per minute.}$$

With the help of these instruments we are able to measure the radiation received per minute at the earth's surface and from this we must calculate the solar constant. Now it follows from Biot's law ($I=I_0\,e^{-\lambda d}$) that the quantity of energy absorbed increases geometrically with the quantity of absorbing material traversed provided it is all under the same physical condition and homogeneous. The loss of radiation due to scattering also follows the same law though the coefficients of direct absorption and of extinction due to scattering are quite different. Nevertheless if I_0 be the initial intensity of the radiation of a given wave-length and aI_0 the intensity after transmission normally through a layer of unit thickness, then the intensity after transmission through a layer m units in thickness can be written as

$$I_m = I_0 a^m. \qquad (69)$$

a is called the coefficient of transparency and generally varies from 0·55 to 0·85. This is in accordance with the well-known law stated for the first time by Bouguer, *viz.*, "For a given coefficient of transmission the quantity of heat transmitted decreases in geometrical progression as the mass of the atmosphere traversed increases in arithmetical progression."

Equation (69) applies strictly to a monochromatic ray and a homogeneous medium. In the atmosphere there is no homogeneity in dust content or in density in a vertical direction but approximate homogeneity exists in a horizontal direction. In the actual experiment the intensity of solar radiation as received on the earth is observed for different elevations of the sun on the same day with constant sky conditions. Then m varies as sec z where z is the sun's zenith distance. Further assuming as a first approximation that a is the same for all wave lengths we can write

$$S = S_0 a^{\sec z} \qquad (70)$$

where S_0, S represent the true and observed solar constant. Then taking logarithms

$$\log S = \log S_0 + \sec z \log a. \qquad (71)$$

Plotting the values of log S as ordinate and the corresponding values of sec z as abscissa we obtain a straight line whose intercept on the ordinate axis will give log S whence S is found.

Langley[1] showed that the value of the solar constant determined in this way would be too low if some of the monochromatic radiations are entirely absorbed by the atmosphere. For an accurate determination of the solar constant, therefore, the following procedure has been found best by Abbot and his collaborators :—

Measurements are made with the spectrobolometer of the relative distribution of energy throughout the spectrum with different solar altitudes but as nearly as possible with constant sky conditions. At the same time the energy of the total radiation of the sun is measured by means of a pyrheliometer. Each portion of the spectrobologram is extrapolated with the help of the Bouguer equation to zero atmosphere and thus the energy distribution curve outside the atmosphere is obtained. The area between the base line (line of zero insolation) and the spectrobolograms for both the actual and the extrapolated curves are found; let these be A and A_0. Then if S be the pyrheliometer reading, the true solar constant S_0 (the extrapolated value) is given by[1]

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[1] See Humphreys, *Physics of the Air*, p. 83.

$$S_0 = S.\frac{A_0}{A}. \qquad (72)$$

According to the measurements made at the Smithsonian Institution since 1902, the mean values of the solar constant are as follows[2] :—

1902—1912	1·933 cal. cm.$^{-2}$ min.$^{-1}$
1912—1920	1·946 „ „

Variation of Solar Constant.—The solar constant has been found to vary by about $\frac{1}{20}$th of its mean value. It is not certain whether these variations are really due to variations in the solar radiation itself or are only due to variations in the composition and transparency of the atmosphere. It is possible however that these variations are connected in some way with sunspots which would presumably produce a change in the amount of total radiant energy emitted by the sun. In fact Ångström found from certain measurements that the solar constant could be connected with the sunspots by the formula

$$S = 1{\cdot}903 + 0{\cdot}011\sqrt{N} - 0{\cdot}0006\, N, \qquad (73)$$

where N is a coefficient (known as Wolf and Wolfer's number) characterising the number and extent of sunspots.

TEMPERATURE OF THE SUN

15·52. Definition.—In sec. 15·12 we discussed the physical divisions of the sun. They are : (1) the *Central Hot Core* terminating in a surface called the photosphere; (2) the *Reversing Layer*, which comes next, and is supposed to contain most of the terrestrial elements in vapour form and gives rise to the Fraunhofer spectrum; (3) the *Chromosphere* which is an extension of the reversing layer, and is due to the ejection of atoms from the reversing layer probably by the action of Selective Radiation Pressure; the chromosphere can be seen only during total solar eclipses, and by special means during day-light; (4) the *Corona*, the nature of which is still unknown, and which until recently, could never be observed except during the brief minutes of a total solar eclipse. But in

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[1] For fuller details of the method, the reader is referred to the original papers of the Smithsonian Institution and particularly to the work "The Solar Constant of Radiation" of G. G. Abbot. Abbot, *The Sun*, may also be consulted for elementary ideas.

[2] For a discussion of more recent data see *Handbuch der Astrophysik*, **4**, p. 83, where the mean value 1·937 is adopted.

1931, B. Lyot constructed an apparatus called the coronagraph by means of which he was able to photograph the inner part of the corona on an observatory at the top of Pic du Midi (height 2860 m.) His success was due to his careful selection of lenses which reduced instrumental scattering to a minimum, and to the fact that at his mountain site, the intensity of scattered skylight was much reduced. The intrinsic intensity of the corona is near about that of the full moon.

These divisions of the sun are based on spectroscopic observations, and probably they are physically not so distinctly marked off from one another as their designations would seem to indicate. Thus we may think that the photosphere is the bounding surface of an enormously heated solid hard core and the reversing layer and the chromosphere are in the same relation to it as our atmosphere is to the solid earth. But the actual facts are not so. The sun (and the same is true of the stars) is a huge mass of gas (mass 2×10^{34} gm.) held together by force of gravitation amongst the atoms. The temperature varies from an enormous value at the centre (10^6—10^7 °C) according to Eddington, 10^9—10^{10} °C according to Milne; it is possible both estimates are wide of the mark to a few thousands on the photosphere which marks the limit of continuous emission. After this, the density becomes so small that gases emit or absorb their characteristic line radiation. There is a flux of radiation from the centre to the surface, the pressure of which counterbalances the pressure due to gravitation and prevents the mass from shrinking beyond a certain limit. The internal constitution of the sun and the stars have formed interesting topics of study by Eddington, Jeans and Milne but is outside the scope of the present book. The reader may consult original papers or Rosseland's *Theoretical Astrophysics*.

From the nature of the problem it is seen at once that the term 'Temperature of the Sun' has rather a vague meaning. We can start by assuming that the term 'photosphere' is really a limiting surface, and has a temperature T_p. This emits radiation which, on analysis, gives us the continuous part of the solar spectrum. The question is how this temperature can be determined.

As the continuous spectrum has to pass through the reversing layer and the chromosphere, it suffers scattering and absorption, and is greatly modified. The effect of these losses is seen if we take a photograph of the sun. The edges appear dark (darkening of the limbs). If the radiation from the centre of the disc is represented by unity for any wavelength, the radiation from a point at a distance x from the centre (x being measured in fractions of solar radius) falls regularly as x tends to 1 (limb of the sun) and ultimately at $x=0·95$ it reaches such low values as 0·48 for $\lambda=3737$, and 0·76 for $\lambda=10080$.

The fall is due to the fact that photospheric light from the limits has to pass through larger thickness of the solar atmosphere (reversing layer and chromosphere), and is more weakened by scattering and absorption than light from the centre. Methods for calculating this loss have been given by Schuster, Schwarzschild, Milne and Lindblad, but for more information on this point the reader is referred to treatises on Astrophysics.

The problem of determining the temperature of the photosphere, and of temperature variation inside and outside of the photosphere is threfore very complex, and can be solved only in successive stages, some of which we now describe.

15·53. Temperature from Total Radiation.—According to careful observations by Abbot and others the solar constant is 1·937 cal. per minute. We can now find out what would be the temperature of a black surface, free from any atmosphere and having dimensions and position of the sun, which would emit the same total radiation at the distance of the earth. This naturally gives us the minimum value for the temperature of the photosphere.

Let the radius of the sun be r, then the amount of heat lost by the sun per second

$$H = 4\pi r^2 .\ \sigma T^4,$$

where T is the *blackbody* temperature of the sun.

If we now describe a sphere of radius R concentric with the sun (R being the distance of the earth), then the energy will be spread over the surface $4\pi R^2$, and hence the amount received per unit surface of the earth is

$$S = \frac{4\pi r^2}{4\pi R^2}.\sigma T^4, \quad \text{or } T^4 = \left(\frac{R}{r}\right)^2 \frac{S}{\sigma}. \quad . \quad . \quad (74)$$

Now r/R=mean angular radius of the sun = $959'' = 4·649 \times 10^{-3}$ radians, $\sigma = 5·77 \times 10^{-5}$ ergs sec.$^{-1}$ cm.$^{-2}$ degree^{-4} and $S = 1·937$ cal. cm.$^{-2}$ min.$^{-1}$

We obtain after substituting these values in (74) that $T = 5732$°K.

15·54. Temperature from Distribution of Energy in the Spectrum of the Sun.—The next question is whether we are justified in assuming that the photosphere of the sun radiates like a black body. For this we have to study the distribution of energy in the spectrum of the sun. This has been done by various workers, and for an account of these works the original articles or treatises in Astrophysics should be consulted. Here we discuss the results only. These have been discussed by Brill[1] and Bernheimer exhaustively and are illustrated in Fig. 34.

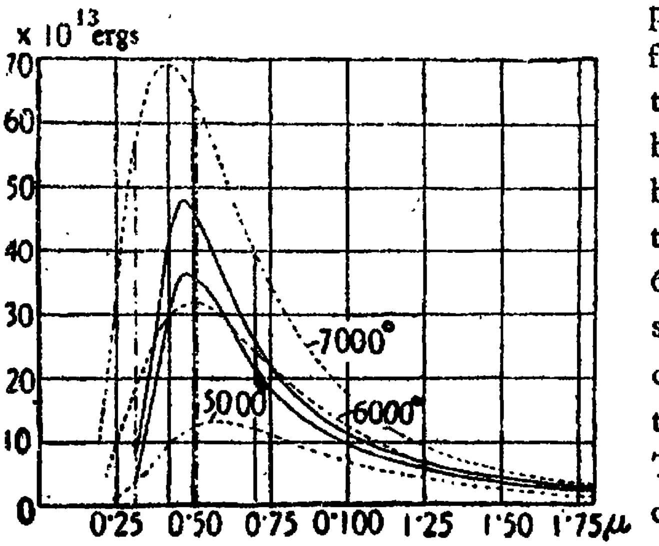

Fig. 34.—Distribution of energy in the solar spectrum.

The full curves represent the observed values of emission for the different wavelengths, the upper curve for radiation from the central part of the disc, the lower for the integrated radiation from the disc. The broken curves represent blackbody radiation for the temperatures 7000°, 6000° and 5000°K. It is seen that the energy curve deviates considerably from that of a black body. Taking the curve for central radiation, we find that from the long wavelength side to about $0 \cdot 78\mu$ the curve can in parts be made to coincide with the curve for 6000°K, but between this wavelength, and the wavelength of maximum emission ($\lambda=4680$), the emission lies between 6000°K and 7000°K. From the wavelength of maximum emission the fall is too steep, and the curve can under no circumstances be made to agree with that for any black body at any temperature. This rapid fall on the violet side is certainly to be ascribed to greater diminution of ultraviolet light by scattering in the atmosphere of the sun, as well as by the terrestrial atmosphere. Below $\lambda=2950$ the solar spectrum entirely disappears though even for a temperature of 5000°K it ought to be continued to $\lambda=2000$. This total absorption has been traced to a layer of ozone which is formed in the upper layers of our atmosphere. Recently[2] by using V2-rockets, spectrographs have been carried upto heights of 110 km., *i.e.*, above the ozone layer, and the solar spectrum photographed to 2099 Å. U.

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[1] *Zeits. f. Physik*, **52**, 767, 1929. *Handbuch d. Astrophysik*, **5/1**, Bottlinger, *same* **2/1**.

[2] *Phys. Rev.*, **70**, 781, 1946; **71**, 827, 1947; **73**, 877, 1948; *Astrophysical J.*, **109**, 1, 1949.

It is therefore fairly certain that the radiation reaching us from the sun differs widely in quality from blackbody radiation. Plaskett investigated the intensity distribution of the light emitted from the centre of the disc and finds that between $\lambda=3800$ and 7600, the radiation is identical with that given by a black body at 6700°K. Wilsing obtains a temperature of 6740°K. But the fact that a certain part of the emission curve can be made to coincide with the curve for a black body can hardly justify the conclusion that the sun emits like a black body. Nothing definite can be said about the character of the photospheric radiation unless the loss for each wavelength due to passage through the sun's atmosphere is definitely determined. But the authors think it unlikely that the emission could be black, because the surface is open, and contains large proportion of free electrons. It is more likely that the emission approximates to that for a metal.

15·55. Temperature from Wavelength of Maximum Emission.—Attempt has been made to determine the temperature from application of Wien's law $\lambda_m T=b$, and the results are given in Table 3.

Table 3.—*Temperature of the Sun from wavelength of maximum emission.*

Observer	λ_m	T°K
Müller and Kron ..	4680	6154
Abbot I ..	4700	6128
Wilsing ..	4820	5975
Abbot II ..	4753	6059

Mean=6079°K.

This temperature is about 300° higher than the temperature deduced from total radiation, but while attaching significance to these values, the reader should bear in mind the considerations presented in the previous paragraphs. See further, *Handbuch der Astrophysik* **4,** article by Bernheimer, p. 48.

15·56. Radiation from the Stars.—The stars are so many suns, only they are at enormous distances compared to the sun. From observations of the spectra of stars, astrophysicists have divided them into a number of classes denoted by the alphabetic letters

$$\mathrm{P}\ldots\underbrace{\mathrm{O}\ldots\mathrm{B}\ldots\mathrm{A}}_{\text{White}}\ldots\underbrace{\mathrm{F}\ldots\mathrm{G}}_{\text{Yellow}}\ldots\underbrace{\mathrm{K}\ldots\mathrm{M}\ldots\mathrm{S}}_{\text{Red}}\ldots\mathrm{R}\ldots$$

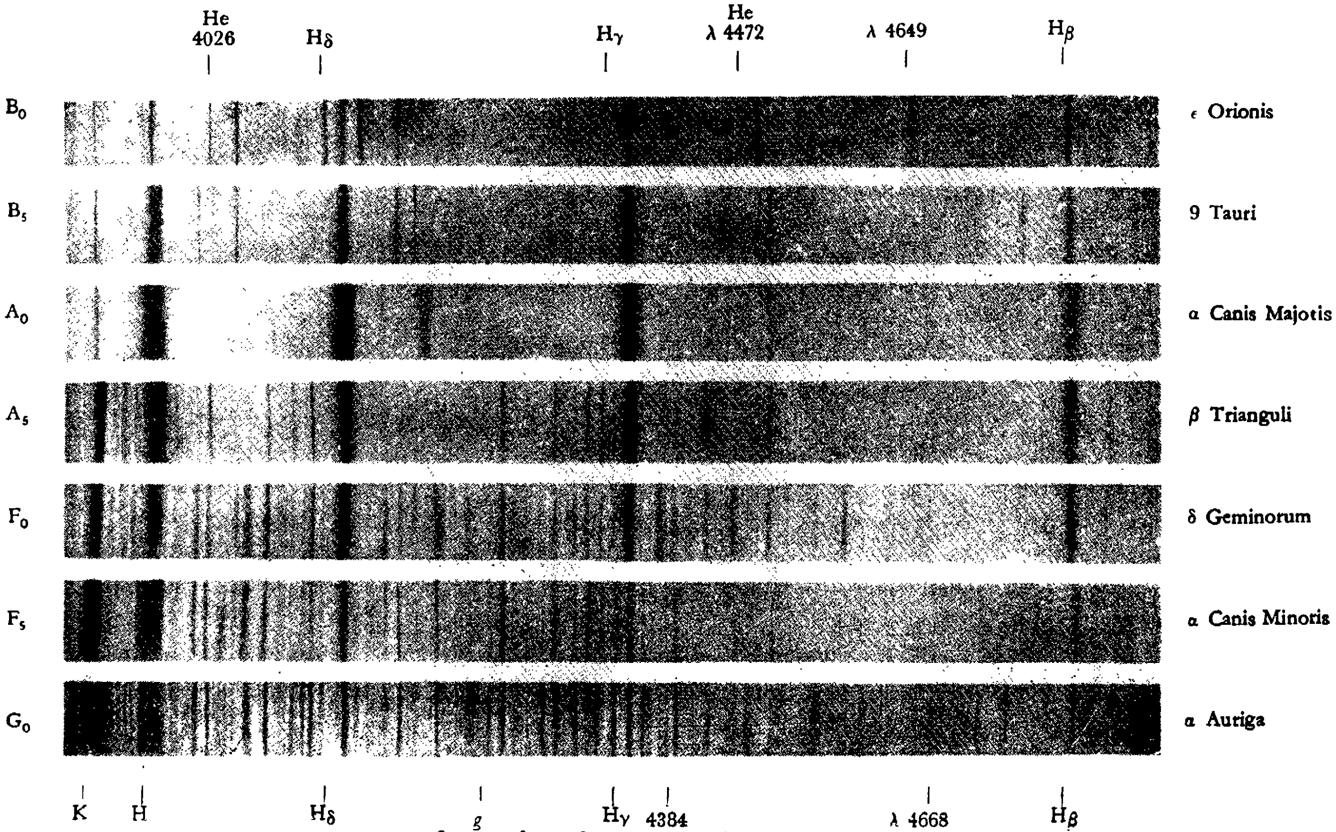
Roughly speaking, the classes O, B, A are white, F and G are yellow, K, M are red to the naked eye. 'P' stars denote nebulae. The classification depends upon differences in the spectra of the stars. The B-stars show the helium lines prominently, while these almost disappear from the A-class, in which hydrogen lines are prominent features. In the F and G classes, metallic lines become more prominent. M, S, R show increasing number of band lines. It is found that the transition from one class to the other is not abrupt, but gradual. This is indicated by a decimal notation. Thus B_5 indicates a star with a spectrum midway between B_0 and A_0 and B_7 a star which is further removed towards A_0.

The determination of the temperature of these stellar bodies is subject to the same uncertainties as mentioned in the case of the sun, and the methods followed are almost identical except that here the total radiation method fails as it is often not possible to determine the diameter of stars. The temperatures are deduced from the distribution of intensity in their emission spectrum by the application of laws of blackbody radiation. The intensities are determined by different experimental methods and the values obtained for stars of different classes by different observers are widely different. The values are reproduced in Table 4.

Table 4.—Temperature of Stars according to different observers.

Spectrum	Wilsing II	King	Sampson	Brill
B 0	12300	22700	25000	23800
B 5	11450	15200	16400	16300
A 0	10250	11600	13100	11800
A 5	9000	8800	10800	9000
F 0	7950	7900	8900	7900
F 5	6880	7000	7400	6900
G 0	5980	6040	6200	6000
G 5	5250	5090	5100	5200
K 0	4570	4570	4200	4570
K 5	3860	3640	3500	3860
M 0	3550	3430	3400	3570

PLATE III



Spectra of stars from B_0 to G_0 class
(For spectra of other classes, see Müller-Pouillet's *Lehrbuch der Physik* Vol. V, part II, from which this plate is reproduced.)

Plate 3 illustrates the spectra of different classes of stars. Father Secchi of Italy was the first to show that stars shining with different colours yield different types of spectra. The subject was taken up by Sir N. Lockyer, and Prof. Pickering and Miss Canon in the Harvard College Laboratory, who undertook an astrophysical survey of the heavens. They photographed the spectra of about two hundred thousand stars and showed that about 95 per cent of stars fall into the six classes designated by the arbitrary sequence of letters, B, A, F, G, K, M. These are elaborations of Secchi's original scheme. The B-stars are white, or bluish-white, and are distinguished by lines of helium; notice the line λ 4472 due to He in the spectrum of B_0. The helium lines disappear in the A_0-class where hydrogen lines are the most prominent. Notice now the transition from A_0 to A_5. The g-line of Ca now appear for the first time. In the F_0-class, more metallic lines are coming out. The G-class corresponds to yellow stars, and their spectra are similar to that of the sun. In the K-stars (sometimes called Antarian from their chief representative Antares) the colour changes to red, and band lines due to TiO are coming out. These are more fully developed in the M-stars which are deep red. Prof. H. N. Russell put forward the view that the varying spectra are due to varying surface temperatures of the stars; this view has been confirmed by the theory of thermal ionisation due to the senior author of this book which gives a unitary explanation of the spectra of stars and also offers views for the temperature radiation of gases.

The temperature of the sun which is a star of the G_0-class is given values ranging from 5890° to 6200°C. But the actual temperature of the photosphere is probably in the neighbourhood of 7000°K. For more detailed information, the above-mentioned article by Brill may be consulted.

PROBLEMS

1. What are the solar constants at Mercury and Mars whose distances from the sun are 0·39 and 1·52 times that of the earth ?

2. When a Féry total radiation pyrometer in a room with surroundings at 300°K is sighted on a black body at 600°K the deflection observed in the galvanometer is 6 divisions. When sighted on another black body the deflection is found to be 400 divisions, calculate the temperature of the latter.

3. If the pyrometer in problem 2 is sighted on a non-blackbody of total emission coefficient 0·8 and the deflection observed is 400 divisions, calculate the temperature of the non-blackbody. Assume

the reflectivity of the body to be the same for radiation at 300°K and at the unknown temperature.

4. For tungsten filament at 1200°K total and spectral emission coefficients for $\lambda=0 \cdot 665\ \mu$ are $0 \cdot 14$ and $0 \cdot 45$ respectively. Calculate the corresponding total radiation temperature and spectral brightness temperature.

Books Recommended

1. Planck, *Wärmestrahlung* or English Translation by Masius.
2. *Handbuch der Experimentalphysik*, Vol. 9, I, pp. 347—474.
3. Jeans, *Report on Radiation and the Quantum Theory.*
4. Jeans, *The Dynamical Theory of Gases*, pp. 348—380 (1925).
5. E. Griffitsh, *Methods of Measuring Temperature* (Griffin, 1947).
6. Burgess and Le Chatelier, *The Measurement of High Temperature.*
7. Abbot, *The Sun.*
8. *Handbuch der Astrophysik*, **4, 5/1.**
9. W. E. Forsythe, *Measurement of Radiant Energy*, McGraw-Hill Book Co. (1937).

CHAPTER XVI

SPECIFIC HEAT OF GASES, LIQUIDS AND SOLIDS

16·1. The elementary theory of specific heat of gases and solids, and its difficulties have been discussed in §3·27. In this chapter, we discuss the attempts at the solution of these difficulties.

SPECIFIC HEAT OF PERFECT GASES

16·2. Specific Heat of Monatomic Gases.—According to the kinetic theory, heat energy of monatomic (spherically symmetrical) substances is entirely due to the translatory[1] motion of the molecules, and $C_v=3R/2$, $C_p=5R/2$, $\gamma=5/3$. The chief monatomic gases investigated are the inert gases and Hg. For them, the above relations should hold up to very high temperatures (about 10000°K), as even at this temperature the electrons cannot be excited. Actually the results have been verified from about −180°C to about 3000°C for argon only and probably they may be found to be true for the other monatomic gases as well. But for substances like Cs, Rb, K, Na, in which the resonance potential is low, and the valency electron is easily excitable, there should be considerable departure from the above values at moderately high temperatures (about 1000°C—2000°C). No experiment appears to have been carried out to test this point.

16·3. Specific Heat of Diatomic Gases.—As already pointed out in §3·23 the diatomic and polyatomic gases will in general possess other types of motion also, in addition to the translational motion. We first take the diatomic molecule. The constituent atoms (say H and Cl in a HCl molecule) may rotate about axes passing through the common centre of gravity or vibrate along the line joining the nuclei. In addition, the electrons may be excited. If these motions are independent of each other (as is usually the case at not too high temperatures), the total energy of a molecule (excluding translation) may be written as

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[1] Rotations can never be produced by mere collision of such molecules with one another if they are smooth spheres initially devoid of rotation and their centre of gravity coincide with their geometrical centre.

$$\epsilon = \epsilon_r + \epsilon_v + \epsilon_e , \qquad \qquad (1)$$

where ϵ_r, ϵ_v, ϵ_e denote energy due to rotation, oscillation and electron displacement respectively.

In the subsequent sections, we give detailed treatment of rotational and vibrational motion of diatomic molecules, but the fullest evidence of the existence of these types of motion is obtained from a study of the band-spectra of molecules. This is beyond the range of this book, and the student is referred to standard books on this subject (e. g. Ruark and Urey, *Atoms, Molecules and Quanta*). Generally it is found that $\epsilon_e > \epsilon_v > \epsilon_r$, so that at ordinary and low temperatures only rotations are excited but with the rise of temperature vibrations are also excited, while the electronic excitation hardly takes place even at the highest temperatures at which experiments are usually done.

16·4. Expression for Energy due to Rotation.—Let us take a diatomic molecule like HCl, consisting of two atoms with the masses m_1 and m_2, separated by a fixed distance r (dumb-bell form). Assuming the motion of the molecule to be governed by classical mechanics, its moment of inertia about its centre of gravity is given by[1] $I = \dfrac{m_1 m_2}{m_1 + m_2} r^2$. The rotational motion can be described by taking three mutually perpendicular axes, one of which is the line joining the two atoms, and the other two are lines perpendicular to this axis and also mutually perpendicular. As the rotation of the molecule about the joining line is incapable of any change by molecular collisions, this motion may be neglected. The molecule has then two degrees of freedom, characterised by rotational motion about the other two axes. The energy is then given by

$$\epsilon_r = \tfrac{1}{2} I (\omega_1^2 + \omega_2^2), \qquad \qquad (2)$$

where ω_1 and ω_2 are the angular velocities of rotation about the two axes.

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[1] Let the two atoms m_1, m_2 be at distances r_1 and r_2 from the centre of gravity. Then $m_1 r_1 = m_2 r_2$; $r_1 + r_2 = r$. Hence $r_1 = r m_2/(m_1 + m_2)$; $r_2 = r m_1/(m_1 + m_2)$ and $I = m_1 r_1^2 + m_2 r_2^2 = r^2 m_1 m_2/(m_1 + m_2)$.

An analytically more correct expression for rotational energy is obtained as follows:—The rotation of the molecule is generally expressed in spherical coordinates by θ and ϕ which are the colatitude and azimuth respectively of the axis of the molecule with reference to an axis fixed in space (Fig. 1). The rotation will be represented by the angular velocity $\dot{\phi}$ in the plane YOX. The precessional motion of the fixed axis of the molecule about the axis OZ is given by $\dot{\theta}$. Hence the resultant linear velocity of the atom at a distance r_1 from the centre of gravity is $(r_1^2\dot{\theta}^2 + r_1^2 \sin^2 \theta . \dot{\phi}^2)^{1/2}$ and the rotational kinetic energy of the molecule is

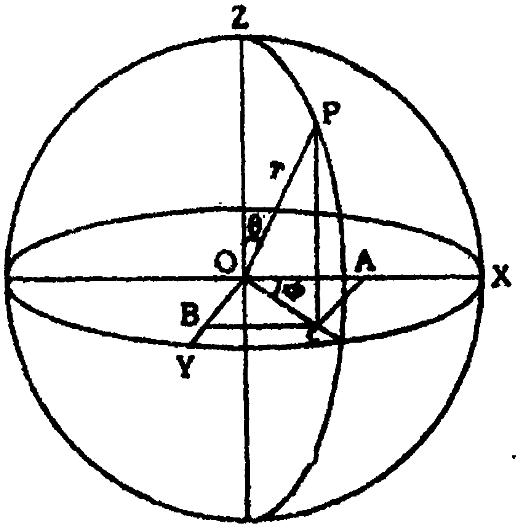

Fig. 1.—Rotation of the molecule in spherical coordinates.

$$\epsilon_r = \tfrac{1}{2}(m_1 r_1^2 + m_2 r_2^2)\,(\dot{\theta}^2 + \sin^2\theta . \dot{\phi}^2)$$
$$= \tfrac{1}{2} I\,(\dot{\theta}^2 + \sin^2\theta . \dot{\phi}^2). \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The corresponding momenta are given by

$$p_\theta = \frac{\partial \epsilon_r}{\partial \dot{\theta}} = I\,\dot{\theta},\ p_\phi = \frac{\partial \epsilon_r}{\partial \dot{\phi}} = I \sin^2\theta . \dot{\phi}$$

so that we have

$$\epsilon_r = \frac{1}{2I}\left(p_\theta^2 + \frac{1}{\sin^2\theta}\, p_\phi^2\right). \quad . \quad . \quad . \quad . \quad . \quad (4)$$

16·5. Energy due to Vibrational Motion.—The vibrational energy due to the oscillation of the nuclei of the component atoms along the joining line is more difficult to find out. As the constituent atoms tend to move further apart from each other, forces of restitution, which are electrical in origin, come into operation. We can suppose these forces to be proportional to the small increase x in the distance between the atoms over the equilibrium distance r_e. Then the equation of motion of the atom of mass m_1 at distance r_1 from the centre of gravity is

$$m_1 \frac{d^2 r_1}{dt^2} = -\mu x.$$

Similarly for the atom of mass m_2 we have $m_2 \ddot{r}_2 = -\mu x$. Hence

$$\ddot{r} = -\mu x \left(\frac{1}{m_1} + \frac{1}{m_2}\right) = -\frac{\mu}{m}\, x,$$

where $r=r_1+r_2=r_e+x$ and m is the reduced mass. Hence

$$m\ddot{r}+\mu x=0. \qquad (5)$$

The frequency of this simple harmonic motion is obtained by solving (5). Its solution is

$$x=A\cos 2\pi\nu t, \qquad (6)$$

where $4\pi^2\nu^2=\mu/m$. The energy of this vibration is

$$\epsilon_0=\tfrac{1}{2}m\dot{x}^2+\tfrac{1}{2}\mu x^2. \qquad (7)$$

Substituting for μ and writing in terms of $p_x=\partial\epsilon/\partial\dot{x}=m\dot{x}$ we have

$$\epsilon_0=\frac{p^2}{2m}+2\pi^2\nu^2 mx^2. \qquad (8)$$

Since in a simple harmonic motion, the energy is once wholly kinetic and once wholly potential, this must also be equal to the maximum kinetic energy of the vibration which is from (6) equal to

$$\epsilon_0=2\pi^2\nu^2 mA^2. \qquad (9)$$

It is more difficult to give any description of the electronic vibrations which will not be attempted here.

If the rotational and vibrational motions are fully excited, the number of degrees of freedom of a diatomic molecule should be 7 (3 due to translation, 2 due to rotation, 2 due to nuclear oscillation).

If the rotational and vibrational motions are fully excited then, from the law of equipartition $C_v=\frac{7}{2}R$, but actually Table 4, p. 105 shows that C_v at moderate temperatures is equal to $\frac{5}{2}R$; hence we conclude that besides translation only two other degrees of freedom are excited for those gases for which $C_v=\frac{5}{2}R$. We shall see that these degrees of freedom are due to *rotation*, as these can be more easily excited than vibration.

16·6. Measurement of the Specific Heat of Hydrogen.—That the classical theory of specific heat fails is seen from the case of hydrogen. The molecular specific heat of H_2 is found to be rather less than the theoretical value $\frac{5}{2}R$ even at room temperatures. Eucken[1] was the first to undertake systematic investigation of the specific heat of hydrogen extending up to very low temperatures, and arrived at the result that C_v gradually sinks down to $\frac{3}{2}$R at about 60°K. Since then, the investigation has been repeated by many workers, and the variation of the specific heat curve with temperature is shown in Fig. 2 and the data are given in Table 3, p. 715, last column. To get the value of C_v, multiply by R and add $\frac{3}{2}$R to the figures given in the last column.

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[1] *Berl. Ber.*, p. 141, 1912.

The general explanation of these curves was originated by Ehrenfest, who pointed out that the rotatory motion (as well as the vibratory motion which we consider later) must be quantised. We have generally

$$C_v = C_t + C_r + C_0 \quad . \quad (10)$$

where C_t denotes specific heat terms due to translation, C_r terms due to rotation and C_0 terms due to nuclear oscillation. Ehrenfest showed that owing to quantisation, C_r and C_0 tend to disappear at low temperatures.

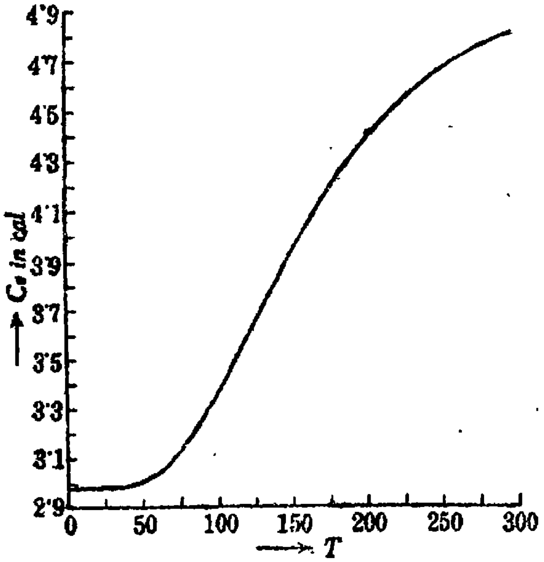

Fig. 2—Variation of specific heat of hydrogen with temperature.

16·7. Quantisation of Rotational Motion.

—We give in this section a brief account of the theory of quantisation of rotational motion due successively to Bjerrum, Schwarzschild, and its further refinement due to application of wave mechanics.

Confining ourselves first to the case where the molecule is supposed to have only one degree of rotation, we have

$$\epsilon_r = \tfrac{1}{2} I\omega^2, \; p_\omega = I\omega, \; \epsilon_r = p_\omega^2/2I. \quad . \quad . \quad (11)$$

We find ourselves now in difficulty, because we must have some method of finding out p_ω. As is well known from dynamics, no problem can be completely solved from the equations of motion alone, or from the integrals which can be deduced from them. A knowledge of initial or boundary conditions is essential. But this is not possible in atomic dynamics, as we cannot subject the atoms or electrons to observation. Some indirect method has to be found.

A lead out of the impasse came out but slowly. Nicholson was the first to observe that the Planck constant h which we introduced in

Chapter XV, has the same dimensions as the angular momentum. Acting on this happy suggestion, Bohr showed that in the hydrogen problem, the moment of momentum of the electron may be put equal to $nh/2\pi$. This enabled him to deduce the Balmer formula for the spectral lines of hydrogen and lay the correct foundation of Atomic Physics (see *Treatise on Modern Physics* by Saha and Saha, Chap. VII).

Following the lead of Bohr, Bjerrum and Schwarzschild put p_ω in (11) equal to $s.h/2\pi$. We then get

$$\epsilon = \frac{h^2}{8\pi^2 I} s^2 = Bhs^2 \, ; \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

where $B = h/8\pi^2 I$.

The correct expression has however been found to be $Bhs\,(s+1)$.

This expression for energy can be obtained by using the space motion of the rotator as described in §16·4, and writing out the wave equation of rotational motion. We have then[1]

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta.\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2\epsilon I\psi}{h^2} = 0. \quad . \quad . \quad . \qquad (13)$$

The characteristic energy-values are given by

$$\epsilon_s = \frac{h^2}{8\pi^2 I} s(s+1) = Bhs\,(s+1). \quad . \quad . \quad . \qquad (14)$$

Vide Dushman, *The Elements of Quantum Mechanics* (1938) p. 149.

The possible rotational energies of the molecule are given by successive integral values of s from 1 onwards. What is the number of molecules in a certain state 's'?

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[1] When the kinetic energy ϵ is expressed in generalized coordinates q as

$$2\epsilon = \sum_{k,l} a_{kl}\, p_k\, p_l,$$

where p_k and p_l are the momenta corresponding to q_k and q_l, then the wave equation is given by

$$D^{\frac{1}{2}} \sum_{k,l} \frac{\partial}{\partial q_k}\left\{ D^{-\frac{1}{2}}\, a_{kl} \frac{\partial\psi}{\partial q_l} \right\} + \frac{4\pi^2}{h^2}\epsilon\psi = 0,$$

where D stands for the operator d/dq, vide *Wave-mechanics*, by De Broglie, p. 83. In this case

$$a_{\theta\theta} = \frac{1}{2I}, \quad a_{\theta\phi} = 0, \quad a_{\phi\phi} = \frac{1}{2I\sin^2\theta}.$$

Hence $$D = \frac{1}{4I^2\sin^2\theta}, \quad D^{\frac{1}{2}} = \frac{1}{2I\sin\theta}.$$

Now equation (13) follows easily.

From a generalisation of Maxwell's distribution law as shown subsequently we can deduce that it is given by

$$N_s = N_0\,(2s+1)e^{-s(s+1)\,Bh/kT} \quad . \quad . \quad . \quad . \quad (15)$$

$(2s+1)=g$, is the weight factor of the sth state. The necessity for multiplying by $(2s+1)$ can be seen in the following way: the rotational quantum number 's' can be represented by a vector s along the axis of rotation. Now if we apply a magnetic field, this axis cannot lie in any direction with respect to the axis of the external field, but can lie only along such directions as make an angle θ with the axis of the field, such that $\cos\theta = m/s$ where m can differ from s only by integral numbers, *i.e.*, the m values are altogether $(2s+1)$ in number, *viz.*

$$m = s,\ s-1,\ \ldots\ldots -s.$$

Thus we find that with reference to the state $s=0$ (non-rotating molecule), the number of orientations of the molecule is $2s+1$. Hence the probability of the existence of the s-molecule is $(2s+1)$.

From equation (15) it follows that the excitation of rotational states with high energy values entirely depends on the values of B and T. At extremely low temperatures practically no rotation can be excited and N_s would have a very small value. If we compare two gases like H_2 and N_2, we find that it is more difficult to excite rotational motion in H_2 than N_2 as B being inversely proportional to the moment of inertia, is larger for H_2 than for any other gas.

At any temperature we shall have the whole assembly of molecules partitioned amongst the states having the quantum numbers $0, 1, 2, \ldots s, \ldots$ but the higher states are not stable. From the principles of quantum dynamics, we know that states with larger energy spontaneously tend to pass to states with less energy, the difference between the two energies being given out as a radiation of frequency ν such that $h\nu = \epsilon_i - \epsilon_f$ where ϵ_i, ϵ_f denote the energy of the initial and final states respectively.

$$\therefore\quad \nu = B[s_i(s_i+1) - s_f(s_f+1)].$$

But actual results show that $s_i - s_f$ cannot have all values. It has been found that $s_i - s_f = \pm 1$ (*The Selection Principle*). Hence putting $s_f = s_i - 1$ we get

$$\nu = B(\pm 2s) \quad . \quad . \quad . \quad . \quad . \quad (16)$$

In the present case only positive transitions have any meaning, hence $\nu = 2Bs$, where

$$B = \frac{h}{8\pi^2 r^2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right). \quad . \quad . \quad . \qquad 17)$$

We find that for hydrogen, and for molecules containing hydrogen (*e.g.*, HCl, HBr, HI, and other hydrides), B will be largest, and substituting probable values ($m_H = 1 \cdot 67 \times 10^{-24}$, $r = a \times 10^{-8}$), we find that $I = 1 \cdot 62 \times 10^{-40} \times a^2$, and ν from (16) becomes equal to $\frac{5 \cdot 1 \times 10^{11}}{a^2} 2s$ for HCl; hence the wave-number $\frac{\nu}{c} = \frac{34}{a^2} s$, and the wavelength $\lambda = \frac{2 \cdot 9 a^2}{s} \times 10^{-2}$ cm. Now 'a' and s are small numbers. Hence the lines due to purely rotational motions lie in the extreme infra-red and are extremely difficult to obtain. But the difficulties in the case of hydrogen halides were overcome by Czerny[1]. The characteristic rotational vibrations were investigated in absorption, because in emission, when a stimulus is applied, the physical state may become different from the normal. The arrangement employed by Czerny is shown in Fig. 3.

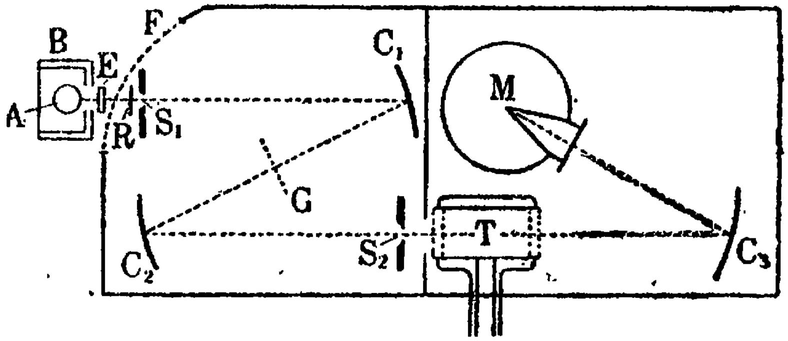

Fig. 3.—Czerny's apparatus for investigating the pure rotation spectrum of hydrogen halides.

A is an Auerburner forming a continuous source of infra-red light which can be cut off if desired by the pneumatically driven shutter E. F is a specially prepared window of Zaponlack membrane while R is a lampblack filter for cutting off short waves, but transmitting very long waves. S_1,S_2 are slits and C_1,C_2,C_3 are concave metallic mirrors of 44 cm. focal length. Gils a wire grating 8×8 cm., grating constant ·3977 mm. for 40 to 70μ and ·7998 mm. for 70 to 100μ. T is an absorption tube containing HCl vapour and is covered by membrane of the same kind as F. M is a radiomicrometer with a sensitiveness of 1100 mm. at a distance of 5 metres with a Hefner candle at a distance of 5 metres. The whole apparatus is placed in a wooden chest which is carefully dried by means of P_2O_5 because H_2O vapour has many absorption bands in the far infra-red.

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[1] *Zeits.f. Physik*, **34**, 227, 1925; **44**, 235, 1927; **45**, 415, 1927.

The beam of rays is collimated by C_1 and falls as a parallel beam on G. The diffracted pencil is focussed by C_2 on the slit S_2, traverses T and is again focussed by the mirror C_3 on the receiver of the radiomicrometer. Deflexion becomes a minimum when the rays are strongly absorbed. The wavelength of the absorbed beams can then be calculated from the relation $\lambda = b \sin\theta$ where θ is read on an angular scale attached to G. The absorption bands represented in Table 1 were obtained for HCl.

Table 1.—*Absorption bands of HCl.*

s	Wavelength in μ	Wave number $1/\lambda$	Successive differences
5	(96·0)	(104·1)	20·49
6	80·45	124·50	20·53
7	68·90	145·33	20·54
8	60·40	165·57	20·20
9	53·83	185·77	20·47
10	48·49	206·24	20·26
11	44·51	226·50	

The wave numbers in column (3) which correspond to the absorption maxima can be represented by the formula

$$1/\lambda = 20{\cdot}8411\, s - {\cdot}001814\, s^2. \qquad (18)$$

Thus the rotational spectrum as obtained by Czerny is in accordance with formula (16), if we neglect the s^2 terms. Since $B = h/8\pi^2 I = 10{\cdot}48 \times c$ in the present case of HCl, we have

$$I = \frac{h}{8\pi^2 \times 10{\cdot}48 \times c} = 2{\cdot}64 \times 10^{-40} = m_H\ (1 - m_H/m_{\text{Cl}}) r^2$$

approximately. Hence r, the distance between the nuclei, $= 1{\cdot}28 \times 10^{-8}$ cm. approximately.

16·8. Contribution of Rotational Energy to Specific Heat.—We have now arrived at the result that an assembly of diatomic molecules can be partitioned, as regards their rotational motion, into a number of quantized states possessing the discrete energy-values $s(s+1)Bh$ and having the weight $2s+1$. Let us take a particular diatomic molecule having its energy of rotation given by the rotational quantum number s. What is the proportion of particles in this state? As shown above this is given by

$$N_s = N_0(2s+1)e^{-\epsilon_s/kT}. \qquad (19)$$

The average rotational energy of the molecules is given by the expression

$$\bar{\epsilon}_r = \frac{\sum \epsilon_s (2s+1) e^{-\epsilon_s/kT}}{\sum (2s+1) e^{-\epsilon_s/kT}}. \qquad (20)$$

To evaluate $\bar{\epsilon}_r$ and C_r we introduce a new function F_r, called the *rotational partition function*, defined by the relation

$$F_r = \sum (2s+1)e^{-\epsilon_s/kT}. \quad \ldots \ldots \quad (21)$$

We have

$$\frac{dF_r}{dT} = \frac{1}{kT^2}\sum(2s+1)\,\epsilon_s\,e^{-\epsilon_s/kT}$$

Hence from the above we get

$$\bar{\epsilon}_r = kT^2\,\frac{d\,ln\,F_r}{dT}, \quad \ldots \ldots \quad (22)$$

and

$$C_r = N\frac{d}{dT}(\bar{\epsilon}_r) = R\frac{d}{dT}\left(T^2\frac{d\,ln\,F_r}{dT}\right). \quad \ldots \ldots \quad (23)^1$$

We can introduce a rotational temperature $\Theta_r = h^2/4\pi^2Ik$. We then find that

$$F_r = \varphi(T/\Theta_r).$$

But there are certain difficulties in the application of formula (23) to actual problems, particularly with respect to hydrogen, which we take up in the next section.

16·9. The Specific Heat of Hydrogen.—Efforts were made by several investigators (Reiche, Schrödinger) to explain the observed C_r values as given by Eucken, with the aid of (23) by assuming some value of B as this was not known. But no single value could be found which would reproduce the results accurately over the whole range. In fact the C_r/T curve for hydrogen was quite different from the curve given by formula (23).

In 1927, T. Hori carried out a complete rotational analysis of the Lyman bands of hydrogen which are obtained in absorption and are, therefore, characteristic of the normal molecule. He

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[1] For high temperatures $(T \gg \Theta_r)$ it can be readily shown that (23) gives the value $C_r = R$. At high temperatures, the terms in (21) corresponding to successive values of s differ so little that the summation can be replaced by integration. Hence

$$F_r = \int_0^\infty (2s+1)\,e^{-Bhs(s+1)/kT}\,ds = \left[-\frac{kT}{Bh}e^{-Bhs(s+1)/kT}\right]_0^\infty = \frac{kT}{Bh},$$

and (23) then gives $C_r = R$.

was the first to find that the value of B was $59 \cdot 534$ cm^{-1} for the fundamental state of H_2, from which I can be easily calculated to have the value $0 \cdot 467 \times 10^{-40}$ gram $\times$ cm^2. This gave the distance between the nuclei in the normal state of the molecule equal to $7 \cdot 6 \times 10^{-9}$ cm. The correct value of B obtained from the spectroscopic analysis when substituted in formula (14) however failed completely to explain the observed values of C_r.

The explanation came from a scrutiny of band-spectrum (molecular spectrum) of diatomic gases consisting of two identical atoms like H_2 or N_2. It was found by Mecke that in these cases, the alternate lines of a band-progression are either absent or very faint. When the atoms are different as in LiH, or unequal in mass, though consisting of the same species as in HD, or N^{14} N^{15}, the phenomenon is no longer observed. The explanation comes from a consideration of the spin of the nuclei of the component atoms. In the case of H_2, the H-nucleus has been shown experimentally to have a spin of $\frac{1}{2}$. When two atoms of hydrogen form a molecule, the nuclei of the two atoms may have their spin-axes either parallel or anti-parallel. The spins of the electrons are always anti-parallel in the normal electron state and make no contribution to the resultant spin of the normal molecule. Ordinary H_2 gas therefore consists of two varieties of hydrogen: (1) a *paraform* in which the nuclear spins are anti-parallel (heteronuclear) and the resultant spin i of the molecule is equal to zero; (2) an *orthoform* in which the nuclear spins are parallel (homonuclear) and the resultant spin i is equal to unity. The statistical weight of *para-molecules* is equal to unity, as it is magnetically neutral while that of the *ortho-molecule* is equal to 3 as it can take up the orientations $i_a = 1, 0, -1$ with respect to external magnetic field. The two forms exist side by side, and one form cannot usually pass on to the other form unless some particular device is used. Dennison[1] therefore contended that we must treat hydrogen as a mixture of two distinct gases, parahydrogen and orthohydrogen whose relative proportions do not alter during the experiments on measurement of specific heat.

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[1] *Proc. Roy. Soc.* A, 115, 483, 1927.

As shown in Note 11 it follows from Pauli's principle that the ortho-molecules can possess only odd-valued rotational quantum states ($s=1, 3, 5 \ldots$) while the para-molecules can possess only even-valued rotational states ($s=0, 2, 4 \ldots$). We have therefore to introduce two different partition functions for the para- and ortho-molecules respectively. These are

$$F_{pr} = \sum_{s=0,2,4} (2s+1)e^{-s(s+1)Bh/kT}$$

$$= 1 + 5e^{-6\sigma} + 9e^{-20\sigma} + 13e^{-42\sigma} + \ldots \quad . \quad (24)$$

$$F_{or} = \sum_{s=1,3,5} (2s+1)\, e^{-s(s+1)Bh/kT}$$

$$= 3e^{-2\sigma} + 7e^{-12\sigma} + 11e^{-36\sigma} + \ldots\ldots \quad . \quad (25)$$

where

$$\sigma = \frac{h^2}{8\pi^2 IkT} = \frac{\Theta}{T} = \frac{84 \cdot 997}{T}. \quad . \quad . \quad . \quad (26)$$

The equilibrium proportion of the paraform to the orthoform can be easily obtained from (15), (24) and (25) if we remember that the statistical weight of orthohydrogen is 3. We have from (15)

$$N_{pr} = N_0\, F_{pr}\,; \qquad N_{or} = 3N_0\, F_{or}.$$

The ratio of N_{pr} to $N_{pr}+N_{or}$ in the equilibrium mixture can be thus calculated and is given in Table 2 and illustrated in Fig. 4.

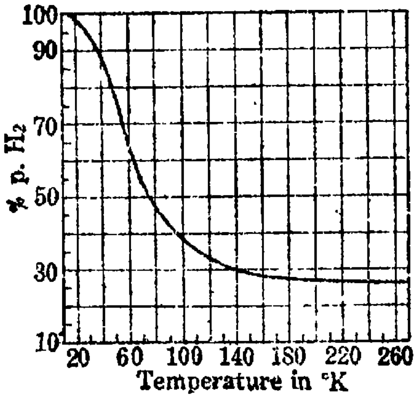

Fig. 4.—Equilibrium percentage of parahydrogen.

Table 2.—Equilibrium proportion of the paraform at different temperatures expressed as percentage of the whole.

T	$\%pH_2$	T	$\%pH_2$	T	$\%pH_2$
20	99·82	60	65·39	140	29·62
22	99·60	70	55·83	160	27·72
25	99·01	80	48·39	180	26·23
30	96·98	90	42·75	210	25·72
40	88·61	100	38·51	230	25·42
50	76·89	110	35·30	250	25·24
		120	32·87	270	25·13

At high temperatures the proportion of ortho-molecules to para-molecules is 3 : 1 but at low temperatures the equilibrium proportion of para-molecules gradually increases reaching nearly 100% at $T=20$°K.

In the usual experiment in the laboratory, however, when we are cooling the ordinary hydrogen gas to low temperatures for specific heat measurements, this equilibrium percentage is not reached. It takes about three years for the process to go half-way under ordinary conditions. The ratio therefore continues to remain as 3 : 1. The equilibrium concentration is reached quickly only when some catalyst is used.

It was on this basis that Dennison explained the results of Eucken. Let us denote by C_{pr} the rotational specific heat of a gram-molecule of para-hydrogen and by C_{or} the corresponding quantity for the ortho-hydrogen. Then we have from (23), (24), (25), (26),

$$C_{pr}/R = \sigma^2 \frac{d^2}{d\sigma^2} \ln F_{pr}, \qquad C_{or}/R = \sigma^2 \frac{d^2}{d\sigma^2} \ln F_{or} \quad . \quad . \quad . \quad (27)$$

These values of C_{pr}/R and C_{or}/R are given in columns 2 and 3 of Table 3. The fourth column contains the quantity C_r/R on the basis that the mixture is made up of 1 part of para- and 3 parts of orthohydrogen *viz.*

$$C_r = \tfrac{1}{4} C_{pr} + \tfrac{3}{4} C_{or}. \quad . \quad . \quad . \quad (28)$$

Table 3.—Calculation of specific heat of hydrogen on the hypothesis of ortho and para forms.

T	C_{pr}/R	C_{or}/R	C_r/R	T	$\frac{C_v - \frac{3}{2}R}{R}$
34	$3\cdot44\times10^{-4}$	2×10^{-8}	$8\cdot6\times10^{-5}$	35	$5\cdot04\times10^{-4}$
42·5	$4\cdot41\times10^{-3}$	1×10^{-6}	$1\cdot1\times10^{-3}$	40	$5\cdot04\times10^{-4}$
51	$2\cdot27\times10^{-2}$	2×10^{-5}	$5\cdot8\times10^{-3}$	50	$1\cdot56\times10^{-2}$
56·7	$4\cdot99\times10^{-2}$	$1\cdot61\times10^{-4}$	$1\cdot26\times10^{-1}$		
68	$1\cdot547\times10^{-1}$	$1\cdot36\times10^{-3}$	$3\cdot98\times10^{-2}$	70	$6\cdot1\times10^{-2}$
85	·4348	$1\cdot06\times10^{-2}$	·117	85	·116
113	1·010	$7\cdot26\times10^{-2}$	·307	110	·323
170	1·467	·382	·653	196	·710
212	1·350	·635	·814		
283	1·116	·882	·941	273	·940

The calculated values of C_{pr}, C_{or}, and C_r are plotted in Fig. 5. Curve No. I stands for the variation of C_{pr} with T, No. II for the variation of C_{or}. The curve No. III represents C_r given according to formula (28). The different signs on it denote the values experimentally obtained by Eucken and others. These values are plotted from columns 5 and 6 which are observed values. The figure shows clearly that the experimental results are in good agreement with the assumption that ordinary hydrogen gas is a mixture of two types of molecules in the proportion 1 : 3.

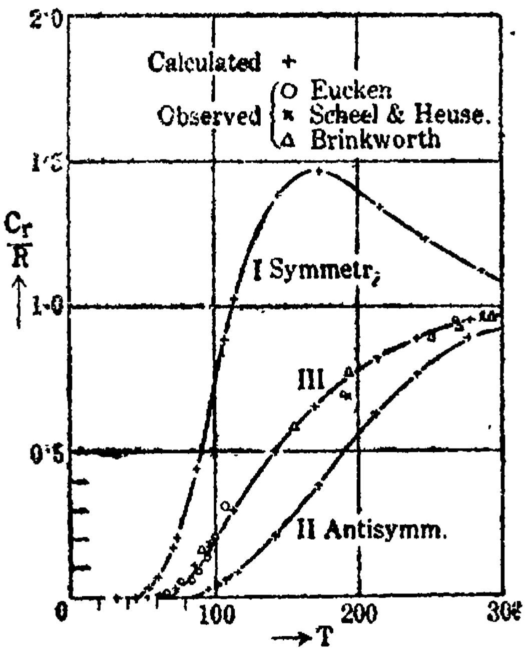

Fig. 5.—Specific heat of hydrogen on the hypothesis of ortho and para forms.

Subsequent works have completely vindicated the hypothesis of Dennison. Bonhoeffer and Harteck have shown that if ordinary hydrogen is passed over activated charcoal placed in a low temperature bath (liquid air, N_2, O_2), it is easily converted into para-hydrogen to the extent of 50%; the conversion becomes 99·8% complete if a temperature of 20°K is used. The process can be thus catalysed by adsorption on charcoal when it takes only a few hours for completion; the time taken by the process in absence of catalysts is a few years. If the temperature is then raised, the gas continues to remain in this paraform for a long time. In this way almost pure para-hydrogen can be prepared and its properties investigated; the properties of orthohydrogen are inferred indirectly by comparing the properties of parahydrogen and normal hydrogen. The physical properties of the para and ortho varieties are completely different as shown in Table 4, where the figure in columns 2, 3, 4 represent vapour pressures in mm. of Hg. The para-gas is a much better conductor of heat than the ortho-gas as it has a much larger C_v. Its band spectra is also different.

Table 4.—Boiling and Triple points of different forms of H_2.

Temperature	Normal H_2	Para H_2	Ortho H_2	Remarks
20·38	760	786·17	752·18	B. P. of nH_2
14·01	53·9	56·8	52·9	T. P. of nH_2
13·80	..	53·0	..	T. P. of pH_2
14·05	..	..	54·2	T. P. of oH_2

For further discussion see *Para, Ortho and Heavy Hydrogen* by L. Farkas, Cambridge, (1935).

16·10. Rotational Specific Heat of other Gases.—In case of molecules composed of two indentical atoms, the successive band lines alternate in intensity in the ratio of $(i+1)/i$ where $i =$ spin quantum number of the nucleus. Thus for N_2 the ratio is 2:1 which shows that $i=1$, *i.e.*, the N-nucleus has the spin quantum number unity. Hence N_2 consists of two forms: para-nitrogen for which $s=0, 2, 4. . ,$ $g_a=(i+1)\times(2i+1)$; ortho-nitrogen for which $s=1, 3, 5. . . .,$ $g_s=i(2i+1)$. The ratio of the number of molecules of these two types at high temperature is $\frac{i+1}{i}=2$. Hence we have generally

$$\frac{C_r}{R}=\frac{1}{g_a+g_s}\left[g_a\,\sigma^2\frac{d^2}{d\sigma^2}\ ln\ F_{pr}+g_s\,\sigma^2\frac{d^2}{d\sigma^2}\ ln\ F_{or}\right].$$

Hence the C_r versus T curve is composed of two curves similar to those in Fig. 5, but as Θ is very small, C_r reaches the value R even at the lowest temperature. Fig. 6 gives a general view of C_r/R curves for a number of gases. The drop in the specific heat at low temperatures has been experimentally observed for two more gases, deuterium (D_2) and HD. For details see Fowler and Guggenheim, *Statistical Thermodynamics* (1939), pp. 91—95.

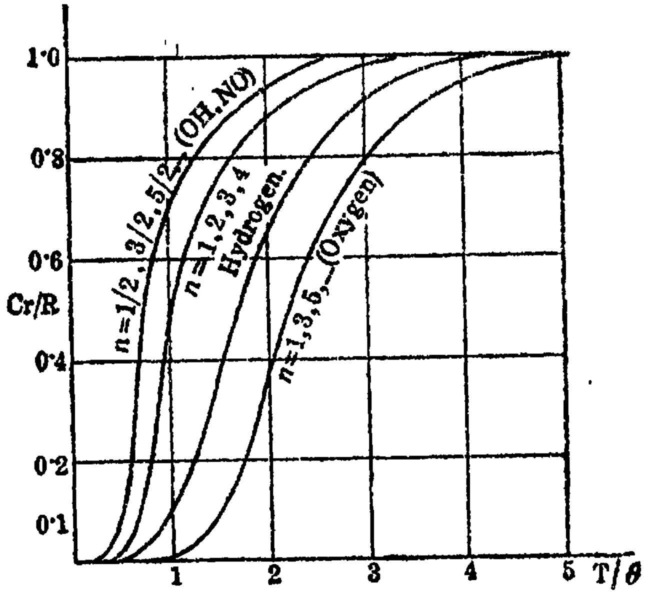

Fig. 6.—Rotational Specific Heat of Different types of molecules.

16·11. Quantisation of Vibrational Motion.—When the temperature is sufficiently great, vibrational motion will also be excited, in addition to the rotational motion. The actual equations of motion are therefore complicated, but we can make a start by neglecting the rotational motion, and considering the simple harmonic motion along the axis of the molecule.

The equation of motion is (p. 706)

$$x=A\cos 2\pi\nu t, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and we get

$$\epsilon_0=2\pi^2\nu^2m.A^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Now it involves the unknown amplitude A. The value of A is obtained from the Sommerfeld quantum-condition

$$\oint p_x \, dx = v.h, \qquad . \quad . \quad . \quad . \quad . \quad (29)$$

where the integration extends over a whole period, and 'v' is an integral number (called Vibrational quantum number). This integral gives us from (6)

$$2\pi^2\nu . \, A^2 m = vh.$$

Hence we have from (9)

$$\epsilon_0 = v. \, h\nu.$$

But this expression was found to be not quite correct. Band analysis showed that

$$\epsilon_0 = (v+\tfrac{1}{2}). \, h\nu. \qquad . \quad . \quad . \quad . \quad . \quad (30)$$

The justification of the last expression for vibrational energy is given by wave-mechanical treatment of equation (5). Replacing p by the operator $(h/2\pi i)\dfrac{\partial}{\partial x}$, we obtain the wave-mechanical equation

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}\left\{ \epsilon_0 - 2\pi^2\nu^2 m x^2 \right\}\psi = 0. \qquad . \quad . \quad (31)$$

It was shown by Schrödinger that this can have analytical solution only when

$$\epsilon_0 = (v+\tfrac{1}{2})h\nu,$$

where 'v' has any integral value 0, 1, 2 etc.

The oscillators can therefore possess the quantized energies

$$\tfrac{1}{2}h\nu, \ (1+\tfrac{1}{2})h\nu, \ldots \ (v+\tfrac{1}{2})h\nu, \qquad . \quad . \quad . \quad . \quad (32)$$

where ν=the fundamental frequency. The frequency of the emitted lines$=(v-v')h\nu$ where v and v' are any two numbers. There is no selection principle for the vibrational quantum number, so that $(v-v')$ may have any integral value. In actual practice, however, the rotational motion is always superimposed on the vibrational motion, and it has been stated that the energy of a molecule in which the vibrational-rotational motion has been excited is given by the sum of the energies due to the two motions separately, *viz.*, by

$$\epsilon = \epsilon_0 + \epsilon_r = (v+\tfrac{1}{2})h\nu_0 + Bhs(s+1). \qquad . \quad . \quad . \quad (33)$$

The frequency of the emitted line is

$$\nu = (v-v')\nu_0 + B\{s(s+1) - s'(s'+1)\}.$$

But $s-s'=\pm 1$, hence

$$\nu = (v-v')\nu_0 \pm 2Bs. \qquad . \quad . \quad . \quad . \quad (34)$$

Equation (34) agrees approximately with the experimental results.

The band corresponding to the transition $v-v'=1$, *i.e.*, $\nu=\nu_0 \pm 2Bs$, where $s=1, 2, \ldots$ is known as the fundamental band. The band corresponding to the transition $v-v'=n$, where n is any positive integral number, is known as the nth upper harmonic. As formula (34) shows, every band consists of a null-point ν_0 (not occupied by any line) with a series of lines symmetrically distributed about it at approximately equal distances $2B$.

The form of the band is illustrated in Fig. 8 which shows the fundamental band of HBr at 3·9μ. It was first investigated by Randall and Imes and has been re-examined by Player and Barker who, in addition to the fundamental, have been able to resolve the first upper harmonic band at 2μ. It should be noted that the effect of rotation is to super-impose a fine structure on the vibration, the distance between the successive fine structure components on the frequency scale giving us the quantity $2B$ which is characteristic of rotational motion.

The experimental arrangement of Player and Barker is shown in Fig. 7.

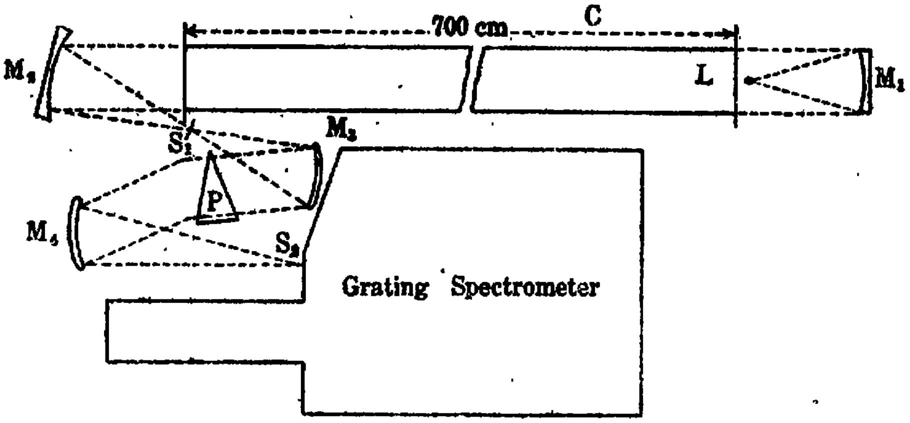

Fig. 7.—Player and Barker's apparatus for investigating the vibration-rotation spectrum of HBr.

C	is the absorption cell which in the case of the fundamental band at 3·9μ was 25 cm. long with windows of NaCl and in the case of the harmonic band was an iron tube 150 cm. long with thin mica windows. The pressure of HBr gas was about 20 cm.
L	is a Nernst glower giving a continuous spectrum.
M_1	is a concave mirror (15 cm. aperture and one metre focal length). The glower is placed at its focal point so that its light is made parallel before passing through the cell.
S_1, S_2	are the slits.
M_2	is another concave mirror which focusses the light on the slit S_1.
M_3	is the collimating mirror.
P	is a rock-salt prism which decomposes the spectrum. Light made parallel by M_3 passes through it.

M_4 is the concave mirror which focusses the light decomposed by the prism on the slit S_2 of the grating spectrometer. The grating has 7200 lines per inch.

The detecting device consisted of a single-junction thermocouple connected to a highly sensitive galvanometer, which in turn actuated a Pfund amplifier.

If the grating alone were used, the first order of λ, the second order of $\lambda/2$, the third order of $\lambda/3$. . . . would have been superposed. The use of the prism P prevents this superposition. The prism alone would have given a very small dispersion. The combined use of the prism and grating ensures good dispersion and separation of spectra of different orders. The frequencies of the component lines of the band are shown in Table 5 and represented according to scale in Fig. 8.

Table 5.—*Fundamental band of HBr at* 3·9 μ.

	s	0	1	2	3	4	5	6	7	8
Positive R	λ (in μ)		3·883	3·859	3·836	3·814	3·795	3·775	3·756	3·731
	ν		2575·55	2591·23	2606·61	2621·35	2685·52	2649·38	2662·60	2675·36
	$\Delta\nu$	32·99	15·68	15·38	14·74	14·17	13·86	13·22	12·76	
Negative P	λ (in μ)		3·934	3·960	3·988	4·017	4·047	4·078	4·110	4·143
	ν		2542·56	2535·51	2507·86	2489·63	2471·36	2452·48	2433.18	2413·30
	$\Delta\nu$	32·99	17·05	17·65	18·23	18·23	18·88	19·0	19·88	

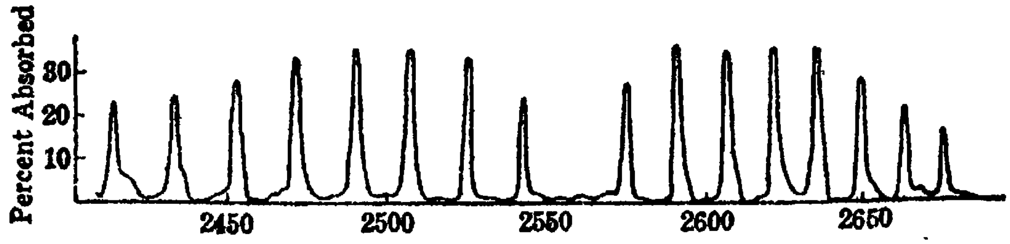

Fig. 8.—Fundamental Vibration-Rotation Bands of HBr.

The frequencies are represented by the formula

$$\nu = 2559 \cdot 26 \pm 16 \cdot 490 s - 0 \cdot 232 s^2 \pm 0 \cdot 0022 s^3, \qquad . \quad . \quad (34a)$$

where $s = 1, 2, 3$. . . . for the successive numbers of the R-branch (positive) and $s = -1, -2, \ldots$ for the P-branch (negative). The square and cube terms in (34*a*) represent interaction between vibration and rotation, and are due partly to change of moment of inertia in the different quantised states.

The frequencies in the case of the harmonic band are represented by the formula

$$\nu' = 5028\cdot 11 \pm 16\cdot 260 s - 0\cdot 449 s^2 \pm 0\cdot 0030 s^3 . \quad . \quad (34b)$$

16·12. Contribution of Vibratory Motion to Specific Heat.

—When a diatomic molecule is excited to its characteristic vibrations, the quantised states are in the simplest cases as proved above, characterized by the energy-values :

$$\tfrac{1}{2}h\nu,\ (1+\tfrac{1}{2})h\nu, \ldots . (v+\tfrac{1}{2})h\nu,$$

where v is any integral number. This picture of the vibrational state of diatomic molecules corresponds to the original one of Planck, proposed for his theory of blackbody radiation, but with the addition of the extra null-point energy $\tfrac{1}{2}Nh\nu$. Let us now calculate the total energy due to vibration. Let N_0 be the number of oscillators with the energy $\tfrac{1}{2}h\nu$, N_v the number with the energy $(v+\tfrac{1}{2})h\nu$. We have from Maxwell-Boltzmann law,

$$N_v = N_0 e^{-vh\nu/kT}. \quad . \quad . \quad . \quad . \quad . \quad (35)$$

The weight-factor is unity. We have now

$$\epsilon_v = \sum_v N_v(v+\tfrac{1}{2})h\nu = \tfrac{1}{2}Nh\nu + N_0\sum_0^\infty vh\nu\, e^{-vh\nu/kT}. \quad . \quad (36)$$

To evaluate ϵ_v let us introduce the *partition function for harmonic oscillators* :

$$F_v = \sum_{v=0}^{v=\infty} e^{-vh\nu/kT} = 1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \ldots = \frac{1}{1-e^{-h\nu/kT}} . \quad (37)$$

Hence

$$N = \Sigma N_v = N_0 F_v \ . \ . \quad . \quad . \quad . \quad (38)$$

From (37), putting $h\nu/kT = x$, we have

$$F_v = \Sigma e^{-vx}; \quad \frac{\partial F_v}{\partial x} = -\Sigma v e^{-vx}.$$

Hence from (36)

$$\epsilon_v - \tfrac{1}{2}Nh\nu = -N_0 \frac{\partial F_v}{\partial x} = -\frac{N_0 h\nu F_v}{F_v}\frac{\partial F_v}{\partial x}$$

$$= -Nh\nu \frac{\partial}{\partial x}(ln\ F_v). \quad . \quad . \quad . \quad (39)$$

Therefore
$$C_0 = \frac{\partial \epsilon_v}{\partial T} = -Nh\nu\frac{\partial^2}{\partial x^2}(ln\ F_v)\cdot\frac{dx}{dT}$$
$$= Nkx^2\frac{\partial^2}{\partial x^2}(ln\ F_v) = R\frac{x^2\ e^x}{(e^x-1)^2}\cdot \quad . \quad . \quad . \quad . \quad (40)^1$$
from (37).

16·13. Calculation of the Specific Heat of Diatomic Gases. —The specific heat of diatomic gases is composed of a rotational part plus vibrational part as stated in §16·3. In the case of all diatomic molecules which do not contain hydrogen, the calculation of the rotational part is only of theoretical interest, as on account of small values of B, $C_r = R$ down to very low temperatures, *i.e.*, even at the lowest temperature employed in these experiments, the rotational degrees of freedom are completely excited. We have therefore to consider only the contribution due to vibrational motion. Table 6 contains the constants[2] characterising rotational and vibrational motion of a few typical gases. With the help of these constants the specific heat of these diatomic gases can be calculated. For detailed comparison of the calculated values with experimental results see Fowler and Guggenheim, *Statistical Thermodynamics* (1939), pp. 98—106.

Table 6.—Molecular Constants for a few Gases.

Substance	H_2	DH	D_2	OH	N_2	O_2	CO	NO $2\pi_1$	Cl_2
ω	4403	3813·75	3114·95	3652	2345·16	1565·37	2167·4	1892·12	564·9
$x\omega$	120·5	90·4	60·3	82·6	14·45	11·37	12·70	14·43	4·0
Θ_0					3374				807·8
B in cm^{-1}	60·87	45·67	30·47			1·44	1·90		·244
$I \times 10^{40}$	·463			1·5	13·8	1925	15·0		114
Θ_r	85			26	2·87	2·0	2·6		·336
i of the atom	1/2			~	1	0	~		
Reference[3]	FZ			Z	Z	Z	Z		

As a first approximation, the value of C_0 (part due to excitation of nuclear oscillations) can be calculated from formula (40) when the

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[1] It can be readily shown that for very large values of T, (40) yields $C_0 = R$.

[2] To obtain Θ_0 multiply ω by 1·43.

[3] F denotes Farkas, *Ergebnisse d. exakten Naturwissenschaften*, **12**, p. 163; Z denotes Zeise, *Zs. f. Elektrochemie*, **39**, 758, 895 (1933); **40**, 3, 663, 885 (1934).

fundamental vibrational frequency of the normal atom is known. But if great rigour is wanted, the anharmonicity of the motion should be taken into account.

The best illustration of the applicability of formula (40) is obtained in the cases of Cl_2, Br_2 and I_2, for which C_v is found to be larger than $\frac{5}{2}$R even at room temperatures. It is due to the fact that owing to their heaviness B is small and rotational degrees of freedom are fully excited giving $C_r = \mathrm{R}$, and as ω happens to be small, the vibratory motion is excited even at room temperature. In such cases, we have

$$C_v = \frac{5}{2}\mathrm{R} + \mathrm{R}\ E(\Theta/T). \qquad . \qquad . \qquad . \quad (41)$$

In Table 7 the values of C_p for chlorine from 243°K to 451°K are given. The second row gives C_0, the contribution due to nuclear oscillation.

Table 7.—Specific heat of Chlorine.

Temp.	243·3 °K	270·2°K	318·4°K	391·4°K	451·7°K
C_p (obs.)	..	7·926	8·118	8·416	8·472
$C_p - \frac{7}{2}\mathrm{R}$	·850	·979	1·170	1·468	1·524
$\mathrm{R}\ E\left(\frac{810}{T}\right)$	·859	·985	1·185	1·405	1·527

Thus the specific heat of chlorine has been satisfactorily explained by assuming $\Theta = 810$, from which $\nu = 1{\cdot}695 \times 10^{13}$, and ω_0 the wave-number $= 565$. This wave-number has actually been found in the analysis of the electronic absorption bands of Cl_2 by Kuhn and Elliot.[1]

The rigorous theoretical calculation in case of Cl_2 is however a difficult and tedious affair, as Cl_2 consists of two isotopes Cl^{35} and Cl^{37} and the molecule is of three varieties 60% $Cl^{35}\,Cl^{35}$; 40% $Cl^{35}\,Cl^{37}$; traces of $Cl^{37}\,Cl^{37}$. The value of ω for $Cl^{35}\,Cl^{35}$ is given in Table 6. The exact calculation has been carried out by Trautz and Ader, but the results obtained are not much different from those calculated from the simple formula (41).

16·14. Specific Heat of Polyatomic Gases.—A polyatomic molecule has several normal modes of vibration depending upon the structure of the molecule. For a linear molecule composed of n atoms the number of these vibrational modes is $3n-5$ while for a non-linear molecule it is $3n-6$. Each of these modes may be regarded as a harmonic vibration and its contribution to the specific heat can be calculated from equation (40) if the characteristic frequency is known experimentally. If the molecule has some element of symmetry, a few of these modes may have identical frequencies and are therefore called degenerate modes. In the calculation of the specific heat the contribution of each degenerate frequency must be multiplied by its weight i.e., number of modes of vibration giving the same frequency. Calculations have been made on this basis for several molecules such as CO_2, N_2O, NH_3, CH_4 etc., vibrational frequencies being determined from observations of infra-red and Raman spectra. For details see, Fowler and Guggenheim *loc. cit.* pp. 107—121.

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[1] *Proc. Roy. Soc. Lond.*, **123**, p. 629.

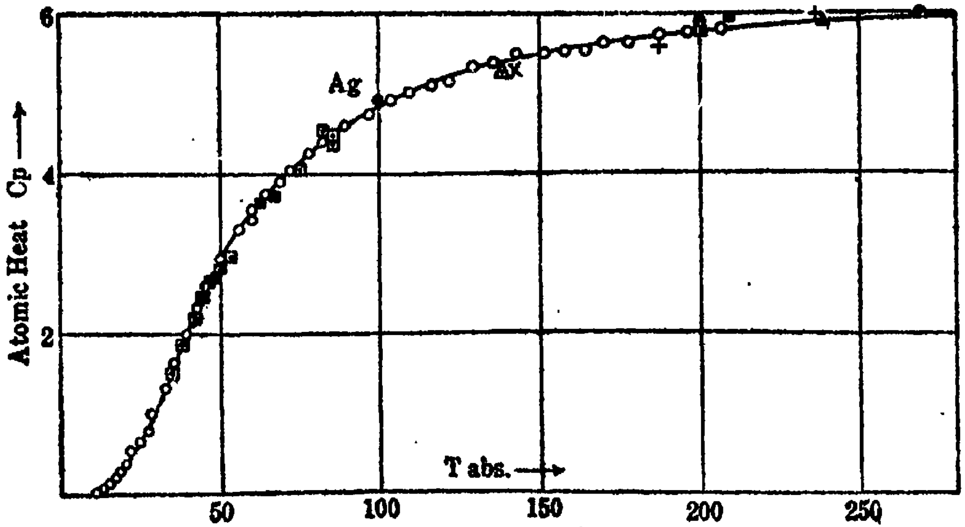
SPECIFIC HEAT OF SOLIDS

16·15. Failure of the Elementary Theory.—The elementary theory of specific heat of solids has been given in Chapter III. There it was mentioned how Dulong and Petit discovered that for all solids $C_v=6$ nearly, and how the relation can be explained from the standpoint of the kinetic theory by the assumptions : (1) A solid consists of atoms, every one of which is regarded as a harmonic oscillator with six degrees of freedom; (2) the mean energy corresponding to each degree of freedom is $\frac{1}{2}kT$ according to the law of equipartition of energy (p. 149); these two assumptions lead us to the result that $C_v=3R$. In chapter VII, p. 331, a method is given for calculating C_v from C_p (equation 20), which is the quantity usually obtained in laboratory experiments, and the values of C_v calculated therefrom are given in Table 3. It will be seen that for many substances, C_v is very nearly equal to $3R$, but for a number of substances, like beryllium, boron, carbon and silicon, C_v was found to be much smaller than $3R$.

Further experiments showed that the failure of the Dulong-Petit law was by no means confined to Be, B, C, Si, *i.e.*, substances with high melting point, but even substances which have normal value of C_v at room temperatures show an abnormal decrease when investigated at low temperature. As we reach absolute zero C_v tends to vanish. This general breakdown was noticed

Table 8.—*Atomic Heat of Silver at different temperatures.*

Temperatures °K	C_v (obs)	C_v calculated from the formula of		Θ calculated from T^3 law	Θ calculated from Debye function
		Einstein (p. 726)	Debye (p. 729)		
1·35	0·000254	$8·76\times10^{-49}$		165	
2	0·000626	$1·39\times10^{-32}$		181	
3	0·00157	$6·16\times10^{-20}$		200	
4	0·00303	$5·92\times10^{-15}$		214	
5	0·00509	$1·62\times10^{-11}$		225	
6	0·00891	$3·24\times10^{-9}$		224	
7	0·0151	$1·30\times10^{-7}$	0·0172	219	
8	0·0236	$2·00\times10^{-6}$	0·0257	216	
10	0·0475	$1·27\times10^{-4}$	0·0502	214	
12	0·0830	0·0010	0·0870	213	
14	0·1336	0·0052	0·137	212	
16	0·2020	0·0180	0·207	211	
20	0·3995	0·0945	0·394	209	
28·56	1·027	0·579	1·014		209
36·16	1·694	1·252	1·69		210
47·09	2·582	2·272	2·60		211
55·88	3·186	2·946	3·22		212
65·19	3·673	3·521	3·73		214
74·56	4·039	3·976	4·13		217
83·91	4·326	4·309	4·45		220
103·14	4·797	4·795	4·68		220
124·20	5·084	5·124	5·17		225
144·38	5·373	5·323	5·37		210
166·78	5·463	5·476	5·51		222
190·17	5·578	5·581	5·61		220



○ Eucken, Clusius and Woitinek; ● Griffiths; + Tilden; X Barschall; ▣ Nernst; ∇ Dewar; △ Behn

Fig. 9.—Variation of Specific Heat of Silver with Temperature

(Taken from Keesom and van der Ende, *Leiden. Comm.* **219*b*, 219*d***).

after methods of determining true specific heats at each temperature were perfected for the low temperature region by Nernst and his coworkers, and by Dewar, Callendar, K. Onnes and others (Chapter II).

For the sake of illustrating this breakdown the data for silver are collected in Table 8. The curve in Fig. 9 shows the values of atomic heat of silver plotted against absolute temperature.

The same failure is shown by almost all metals and non-metals investigated. For the sake of completeness it may be mentioned that even substances like boron and carbon tend towards the theoretical value of 3R at high temperatures. In the case of diamond this value is attained at about 980°C.

16·16. Quantum Theory of Specific Heat.—The first attempt to explain these anomalies was made by Einstein[1] (this was the first instance of application of quantum theory to problems of specific heat) in 1907. Einstein pointed out that the average energy of an oscillator vibrating with the frequency ν is not kT per degree of vibration, but as explained on p. 671, it is given by the formula[2]

$$\frac{h\nu}{e^x-1}, \qquad \qquad (42)$$

where $x=h\nu/kT$. He assumed that a solid like Ag is a collection of atomic vibrators characterised by one and the same frequency (*monochromatic vibrations*). Under this assumption the total energy-content of a gram-atom of the solid consisting of N atoms is

$$U=3N.\frac{h\nu}{e^x-1}. \qquad \qquad (43)$$

We have then

$$C_v=\frac{dU}{dT}=3R.\frac{x^2e^x}{(e^x-1)^2}. \qquad \qquad (44)$$

as in (40). It is easy to see that for large values of T, equation (44) gives $C_v=3R$ in agreement with Dulong and Petit's law. Also at

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[1] *Ann d. Physik*, **22**, 180, 800, (1907); **34**, 170, 590 (1911).

[2] Addition of the extra null-point energy $\frac{1}{2}h\nu$ as on p. 721 makes no difference to the specific heat as it will cancel out on differentiation (see §16·12).

$T=0, C_v=0$, *i.e.*, at the absolute zero the atomic heat falls to zero, a conclusion in general agreement with experimental results.

Now x can be written in the form Θ/T, where $\Theta=h\nu/k$, and therefore $C_v=3R.\,E(\Theta/T)$, where $E(x)=\frac{x^2e^x}{(e^x-1)^2}$. Since Θ is assumed to have a fixed value for a particular substance, this expression gives the variation of atomic heat with temperature. For different substances different values of ν and Θ had to be assumed, and these were obtained purely empirically in order to fit with the experimental results. The function $E(\Theta/T)$ is generally known as the Einstein function and is usually denoted by $E(x)$. A table of values of $E(x)$ from $x=0$ to $x=17$ is given in Note 12 and the course of the curve $E(x)$ is shown in Fig. 10 along with a curve calculated from Debye's formula (sec. 16·17). It will be seen that the Einstein expression explains the specific heat curves up to a certain point, but fails completely at extremely low temperatures (*vide* Table 8 second and third columns). For silver at 14°K, the value calculated from Einstein's formula is 28 times lower than the experimental value and at lower temperatures the discrepancy is greater. Another weak point in Einstein's deduction is that ν and Θ are obtained empirically and cannot be verified from any other independent physical data. Nevertheless it was a great step forward in the right direction.

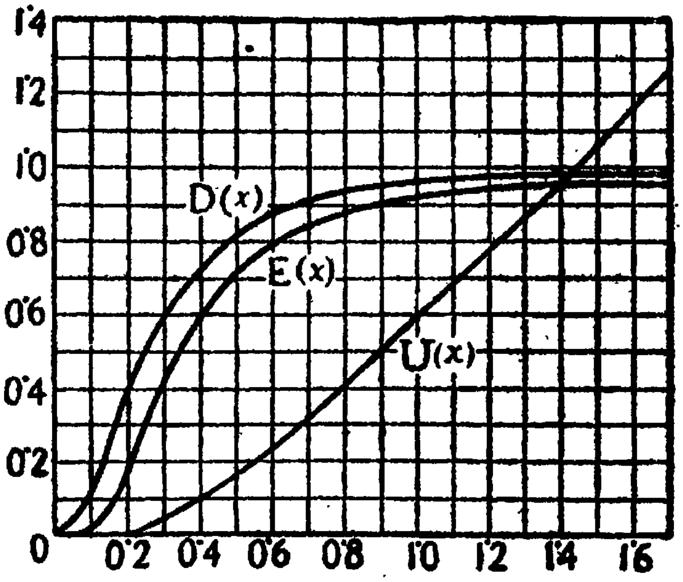

Fig. 10.—Curves representing Einstein and Debye functions.

Einstein[1] himself recognized that the assumption of monochromatic vibrations did not correspond to actual facts. The vibrations of a particular atom must be very complex indeed because it is under the field of force of thousands of other vibrating atoms.

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[1] *Ann. d. Physik*, **35**, 779, 1911.

16·17. Debye's Theory of Specific Heat of a Solid.—The problem was next attacked by Debye[1]. He concluded from the nature of the problem that (1) the vibrations would form a continuous spectrum; (2) these vibrations are identical with the elastic vibrations of a continuous solid (acoustical vibrations).

When a continuous solid is thrown into elastic vibrations, two kinds of waves are excited in it: (*a*) transverse vibrations, which travel with the velocity $c_t = \sqrt{n/\rho}$ and (*b*) longitudinal vibrations which travel with the velocity $c_l = \sqrt{(k + \frac{4}{3}n)/\rho}$, where n is the coefficient of rigidity and k the bulk modulus. The number of modes of vibration of kind (*b*) contained between the frequency limits ν and $\nu + d\nu$ and enclosed in the volume V is[2]

$$= \frac{4\pi\nu^2 d\nu}{c_l^3} \cdot V, \quad \ldots \quad (45)$$

and the number of modes of kind (*a*) between the same limits

$$= \frac{8\pi\nu^2 d\nu}{c_t^3} V. \quad \ldots \quad (46)$$

In the second case the expression has been doubled, as each torsional wave is two-sided, or is equivalent to two waves polarized at right angles to each other. The total number of independent modes of vibration is now given by

$$\int_0^{\nu_m} 4\pi V \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \nu^2 d\nu. \quad \ldots \quad (47)$$

The upper limit of integration cannot be infinite, as this would make the number of degrees of freedom infinite. Actually this number is $3N$, where N is the number of particles. This enables us to obtain ν_m by putting the integral (47) equal to $3N$. This gives us

$$\nu_m^3 = \frac{9N}{4\pi V \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right)}. \quad \ldots \quad (48)$$

The elastic spectrum was thus guillotined by Debye at an upper limit ν_m which has a definite value for each substance.

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[1] *Ibid*, **39**, 782, 1912.

[2] See p. 666.

Let us now calculate the energy of the solid. Since the mean energy of a wave of frequency ν is, by Planck's theorem, $h\nu/(e^{h\nu/kT}-1)$, we have

$$U = 4\pi V\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)\int_0^{\nu_m}\frac{h\nu^3 d\nu}{e^{h\nu/kT}-1}. \qquad (49)$$

Combining with (48) we have

$$U = \frac{9N}{\nu_m^3}\int_0^{\nu_m}\frac{h\nu^3 d\nu}{e^{h\nu/kT}-1}. \qquad (50)$$

To evaluate this expression, let us put

$$h\nu/kT = \xi,\ h\nu_m/k = \Theta, \text{ and } \Theta/T = \xi_m = x. \qquad (51)$$

Then

$$U = 3RT.\ 3\left(\frac{T}{\Theta}\right)^3\int_0^{\xi_m}\frac{\xi^3 d\xi}{e^{\xi}-1}. \qquad (52)$$

This expression cannot be integrated in finite terms.

Again, differentiating (50) with respect to T and making substitutions as above, we have

$$C_v = \frac{9R}{x^3}\int_0^x \frac{\xi^4 e^{\xi} d\xi}{(e^{\xi}-1)^2}. \qquad (53)$$

It is easily seen that

$$\int_0^x \frac{\xi^4 e^{\xi}}{(e^{\xi}-1)^2}d\xi = -\left[\frac{\xi^4}{e^{\xi}-1}\right]_0^x + \int_0^x \frac{4\xi^3}{e^{\xi}-1}\,d\xi.$$

Therefore

$$C_v = 3R\left[\frac{12}{x^3}\int_0^x \frac{\xi^3 d\xi}{e^{\xi}-1} - \frac{3x}{e^x-1}\right]. \qquad (54)$$

This is the Debye expression for the atomic heat of a monatomic solid but unfortunately it cannot be evaluated in finite terms. The expression within square brackets is a function of x only and may be denoted by $D(x)$. It is usually known as the Debye function and has been calculated[1] for values of x ranging from 0 to ∞ (*vide* Note 12). Let us first consider some limiting cases.

(1) When T is very large, x and ξ are very small and the expression then simplifies to $C_v = 3R$.

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[1] See Debye, *Ann. d. Physik*, **39**, 789, 1912.

(2) At very low temperatures T is very small and therefore x and ξ are large. The second term in (54) becomes negligible since with increasing values of x, the exponential factor in the denominator increases much faster than the numerator. Again the denominator in the first term is large unless ν is small. Thus terms containing large ν contribute little to the total atomic heat; *i.e.*, energy is concentrated in the spectrum of lower frequencies. Hence we can replace the upper limit x in (54) by ∞. We have then

$$C_v = 3R. \frac{12}{x^3}\int_0^\infty \frac{\xi^3\, d\xi}{e^\xi - 1}.$$

The value of the integral is $\pi^4/15$ (see p. 672). Hence

$$C_v = 3R. \frac{12\pi^4}{15}\left(\frac{T}{\Theta}\right)^3 = 77\cdot 94 \times 3R\left(\frac{T}{\Theta}\right)^3. \qquad (55)$$

Since Θ is a constant for the substance, the specific heat at extremely low temperatures varies as T^3. This is known as *Debye's T^3-law.*

This law has been verified for a number of substances. The data[1] for calcium fluoride[2] (CaF_2) are given in Table 9. The first column gives the temperature, the second column the observed atomic heat C_v and the third column the value of $100\sqrt[3]{C_v}/T$. It will be seen that the figures in column (3) are constant, thus illustrating the validity of the T^3-law.

Table 9.—Illustration of Debye's T^3-law.

T	C_v	$100\dfrac{\sqrt[3]{C_v}}{T}$
17·5	0·0670	2·32
19·9	0·1028	2·36
21·5	0·1316	2·37
23·5	0·1680	2·35
25·6	0·2180	2·35
27·6	0·276	2·36
29·1	0·331	2·38
34·0	0·536	2·39
36·8	0·663	2·37
37·8	0·713	2·38
39·8	0·836	2·37

Again, assuming the T^3-law, we can calculate the value of the characteristic temperature Θ with the help of (55) from values of C_v at low temperatures. For

$$\Theta = \left[\frac{77\cdot 94 \times 5\cdot 975}{C_v}\right]^{\frac{1}{3}} T$$

$$= 7\cdot 745\ T C_v^{-\frac{1}{3}}. \qquad (50)$$

The values of Θ so calculated are given in the fifth column of

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[1] See Eucken and Schwers, *Verb. d. D. Phys. Ges.*, **15**, 578, 1913.

[2] For substances containing many atoms in a molecule the atomic heat is found by dividing the molecular heat by the number of atoms in the molecule.

Table 8. Note that as T increases, Θ no longer remains constant as the T^3-law then fails to hold.

When $T=0$, (55) gives $C_v=0$, *i.e.*, the atomic heat vanishes at the absolute zero.

16·18. Comparison of Debye's General Formula with Experimental Results.—It is seen from equations (54) and (51) that for all solid isotropic bodies, we can find out a characteristic temperature $\Theta=h\nu_m/k$ such that the atomic heat at any temperature is then simply given by

$$C_v = 3R.\ D(x), \qquad \qquad . \quad . \quad . \quad (57)$$

where D represents the Debye function. If we now plot C_v against $1/x=T/\Theta$ we shall get a curve[1] which will be identical for all isotropic bodies. Hence if the specific heat/temperature curve for any metal be known, that for any other substance can be obtained by a point to point correspondence in which the ordinate C_v is the same, but the abscissæ are changed in the ratio of Θ_1 to Θ_2 *i.e.*, C_v obeys a law of "corresponding states." This is illustrated in the curves shown in Fig. 11.

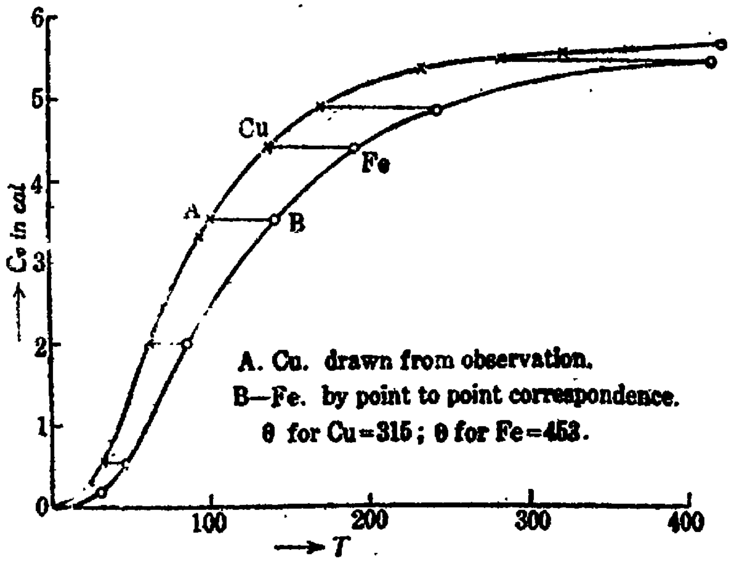

Fig. 11.—Correspondence between atomic heat curve for iron and copper.

The curve representing the variation of atomic heat of copper with temperature is drawn from the observed values while the curve for iron is drawn from the Cu-curve in the above-mentioned way. To the point A on the Cu-curve corresponds the point B on the Fe-curve and so on.

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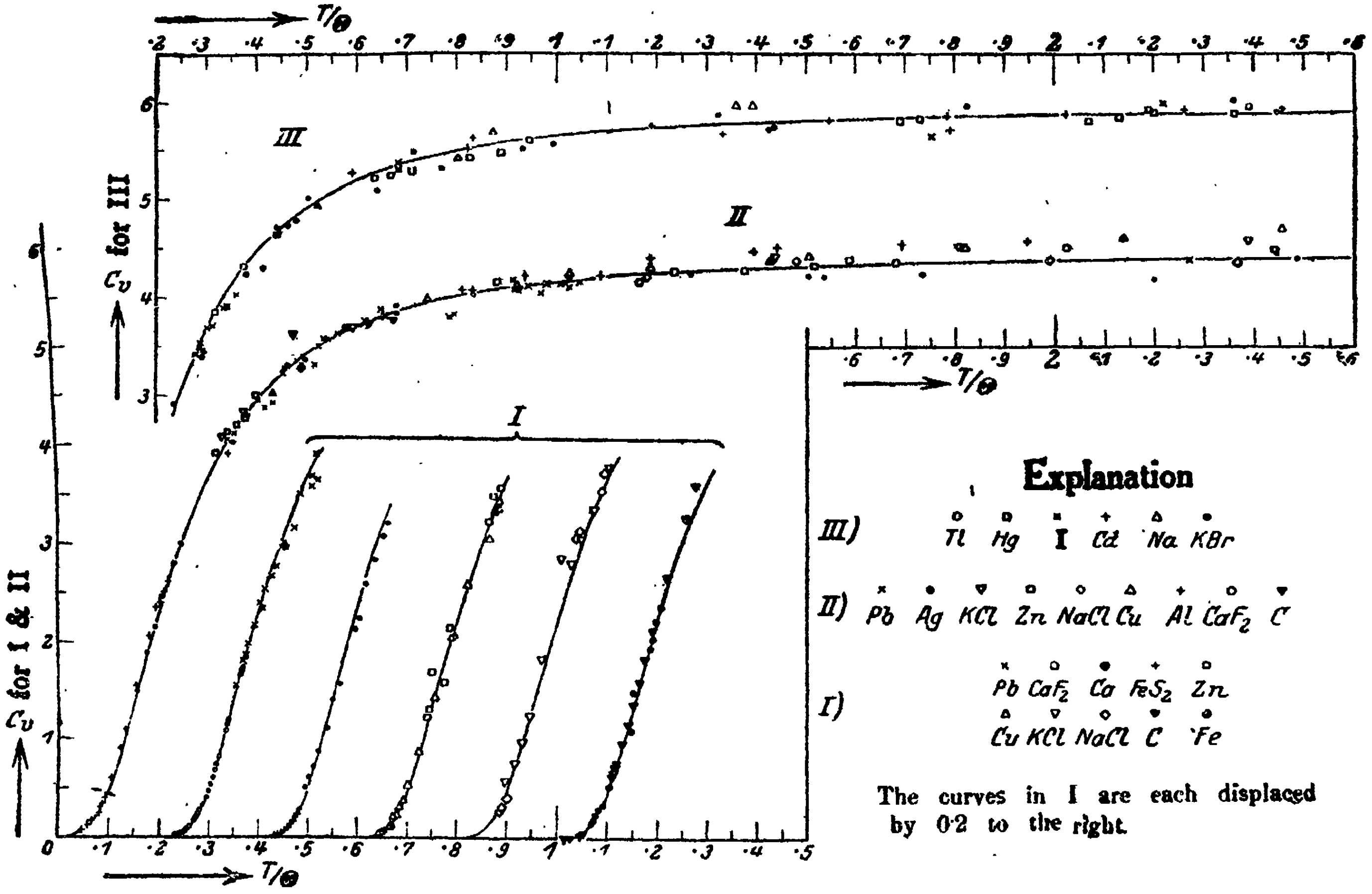
[1] For methods of finding Θ see later in this section.



The curves in I are each displaced by 0·2 to the right.

Fig. 12.—Experimental verification of Debye's theory of specific heat.

The data for a very large number of substances are represented by means of curves in Fig. 12, in which C_v is plotted as ordinate

Table 10.—*Values of* Θ *for different substances.*

Substance.	Curve	Temp. range for C_p.	Θ from C_p-data.	Θ Elasticity data	Θ T^3-Law	Θ Thermal Expansion	Θ Residual Rays	Reference
Li			510					S
Na	III		202					B
K			126					LB
Rb			~85					"
Cs			~68					"
Cu	I, II	14—773	315*	341	321	325		B
Ag	II	1—433	218	220	217	210		
Au			175					LB
Be		10—300	800-1000					S
Mg			290					LB
Ca	I	22—62	226					"
Zn	I, II	33—673	235					"
Cd	III		168*	174				D
Hg	III		97					
Al	II	19—773	396*	399*		374		D
Tl	III		96					
C	I, II	30—1160	1860		2330	1860		
Ge		10—200	290					S
Sn			119					LB
Pb	I, II	19—573	88*	72*				D
I	III		106					
Bi			111					
Fe	I	30—220	332-410	483	455	413		D
Ni			375					S
W		>300	310					LB
CaF_2	I, II	17—328	474	510			645	Z
FeS_2	I	22—57	645	696				
NaCl	I, II	22—666	281	305			281	
KCl	I, II	23—547	230	227			230	
KBr	III		177				177	

S—denotes Simon and his pupils, *Zs. f. ph. Chem.* (B), 25, 273-282 and other papers. B = Bethe, *Handbuch d. Physik*, **24/2**, 524. L. B. = Landolt-Börnstein's *Tables, Ergänzungsband*, 1232. D = Debye, *Ann. d. Phys.*, **39**, 789, 1912. M = Mott, *Proc. Phys. Soc.* **46**, 680, 1934. Z = Zwikker; *Zs. f. Phys.*, **52**, 668, 1929. In cases where Θ's are given from more than one method, the source in the last column refers to those marked with asterisk.

and T/Θ as abscissa. The curves are due to E. Schrödinger,[1] and illustrate remarkably well the validity of Debye's law of atomic heats.

Explanation of the curves.—The continuous line in these curves is a theoretical Debye curve and the points marked +, △ etc. stand for the observed values of C_v for different substances. Thus in curve II which is a full Debye curve, + stands for Al the values for which extend from $T/\Theta = \cdot 04$ ($T = 191$°K where $C_v \doteq \cdot 066$) to $T/\Theta = 1\cdot 95$ ($T = 773°$, $C_v = 5\cdot 6$). Similarly × stands for Pb, △ for Cu, □ for Zn, and so on. It will be seen that the observed values lie remarkably close on the theoretical curve. As it is impossible to represent the points for all substances on the same curve without causing confusion, portions of the curve are redrawn separately (curves I and III) and slightly displaced to prevent overlapping. The points for some substances are marked on these separate portions. The series of curves in I are each displaced to the right by 0·2 while the curve III is displaced vertically by 1·5. It will be thus seen that the atomic heat values of a very large number of substances is given by Debye's law. The values of Θ used for different substances plotted in the various curves are given in Table 10.

Calculation of the Debye Maximum Frequency.—It may be mentioned here that for every substance, that value of Θ is selected which fits best the atomic heat/temperature curve obtained experimentally. The values of Θ so obtained are given in column 4 of Table 10. But Θ may be obtained from the T^3-law (equation 56). These values are given in column 6.

We can however calculate Θ independently of atomic heat determinations, *i.e.*, from the elastic constants of the substance. For $\Theta = h\nu_m/k$ where ν_m is given by (48).

$$\therefore\ \Theta = \frac{h}{k}\left[\, 9N \Big/ 4\pi V \left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right)\right]^{\frac{1}{3}} \qquad . \quad . \quad (58)$$

Now the velocities c_l, c_t are given by the relations

$$c_l = \sqrt{(k+\tfrac{4}{3}n)/\rho}, \qquad c_t = \sqrt{n/\rho},$$

where n and k respectively denote the rigidity and bulk modulus of elasticity of the substance, and ρ its density. Hence

$$\Theta = \frac{h}{k}\left(\frac{9N}{4\pi V}\right)^{\frac{1}{3}} \rho^{\frac{1}{2}} \left[\frac{1}{(k+\frac{4}{3}n)^{3/2}} + \frac{2}{n^{3/2}}\right]^{\frac{1}{3}} \qquad . \quad . \quad . \quad (59)$$

The values of Θ calculated in this way are given in column 5 of Table 10.

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[1] *Phys. Zeits.*, **20**, 420, 450, 474, 497, 523, 1919.

Θ can also be calculated from the thermal expansion with the aid of Grüneisen's relation between α and C_p. The values so calculated are given in column 7, while the last column gives Θ calculated on the assumption that $\nu_m = \nu_r$ the frequency of Reststrahlen.

The values of Θ calculated from the specific heat data and from the elastic data agree tolerably well for a number of substances, but the agreement is not quite satisfactory. It may be remarked that the elastic constants vary with temperature and a better agreement might be expected if the values at low temperatures are used. Eucken however found that the agreement then becomes worse rather than better.

16·19. Modifications of Debye's Theory.—Though Debye's theory is fairly successful in accounting for the variation of specific heat of solids in a general way, it is difficult to agree with its theoretical foundations. The two fundamental assumptions are :

(a) When a solid is heated it is supposed that elastic vibrations[1] like those of a *continuous* medium exist within the body, having frequencies from 0 to a certain maximum ν_m given by (48) where the spectrum is guillotined sharply. Even if a solid be isotropic, it cannot be treated as a continuum since it is composed of atoms separated in space.

(b) The solid is regarded as an *isotropic* body, while actually solids are composed of definite crystals, either in the form of single crystals, or minute crystals brought together by pressure. No account is taken of the crystalline structure in Debye's theory.

Slater[2] has given a discussion of (a). On account of the atomic nature of the solid eqn. (48) becomes incorrect for two reasons :—(1) The velocity of the elastic vibration depends upon the wavelength (shorter waves travelling slower) when the wavelength of the vibration is comparable with the atomic distances (as it is for frequencies approaching ν_m) and hence the change of velocity with frequency must be taken into account in formulating (48). (2) In an actual solid composed of N atoms we have to find the normal or independent modes of vibration of the atoms in the solid. The problem was solved by Born[3] by assuming "periodic" boundary conditions or assuming fixed boundaries, the force between atoms to be given by Hooke's law. He showed that there will be $3N$ normal modes of vibration. Thus the total number of modes comes out to be the same as the number of degrees of freedom of the solid as assumed by Debye, but the frequency distribution assumed by Born is different from Debye's even for an isotropic medium. This can be easily seen without going into the details of Born's theory.

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[1] Only a few of these elastic vibrations will be in the audible range and ν_m generally lies in the infrared region. The lower acoustic vibrations and hence the solid in thermal equilibrium would be audible had it not been for the fact that the energy in these vibrations is too low.

[2] See *Introduction to Chemical Physics*, Chap. XIV.

[3] Born and Kārmān, *Phys. Zeits.*, **13**, 297, 1912; **14**, 15, 1913; Born, *Dynamik der Kristallgitter* (Leipzig, 1916).

In a solid composed of atoms it is evident that the highest overtone permissible cannot have wavelength shorter than interatomic distance d, for the displacement etc. of atoms for waves of length less than d can be as well represented by longer waves and hence these vibrations are not really independent. This shows that in a linear array of atoms the normal modes have the wavelengths d, $2d$, $3d$ . . . , and are thus equal to the number N of atoms in the array. For a three-dimensional solid consisting of N atoms this will also be N, but each of these vibrations may be longitudinal or transverse of either type of polarisation; hence the total number will be $3N$. As explained above, the highest overtone is not limited by an identical ν_m for both longitudinal and transverse vibrations as assumed by Debye, but by an identical λ for both types of vibrations as pointed out by Born. Since the longitudinal wave velocity is greater than the velocity of transverse waves, the maximum permitted ν_m for longitudinal waves (viz. $\nu_{m,l}$) is greater than $\nu_{m,t}$ for the transverse waves. Thus following Born we must integrate only upto a minimum value λ_m given by the relation[1]

$$4\pi(1/\lambda_m)^3 V = 3N. \quad . \quad . \quad . \quad . \quad (60)$$

This λ_m gives the corresponding $\nu_{m,l}$, $\nu_{m,t}$ from the relations $c_l = \lambda_m \nu_{m,l}$, $c_t = \lambda_m \nu_{m,t}$. Thus we must integrate (53) upto $\nu_{m,l}$ and $\nu_{m,t}$ for the longitudinal and transverse waves respectively rather than over a common ν_m as done by Debye. Evidently the specific heat comes out to be

$$C_v = \mathrm{R}[D(\Theta_l/T) + 2\,D(\Theta_t/T)], \quad . \quad . \quad . \quad (61)$$

where $\Theta_l = h\nu_{m,l}/k, \quad \Theta_t = h\nu_{m,t}/k.$

Another correction of somewhat lesser importance arises from the fact that the evaluation of the modes of vibration as given on p. 666 viz. eqn. (39a) is correct only when the ellipsoid lies within the permitted values of n_1, n_2, n_3, the maximum permissible values of n_1, n_2,

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[1] From (45) the number of modes of vibration between the frequencies 0 and ν is $\frac{4}{3}\pi(\nu^3/c^3)V = \frac{4}{3}\pi(1/\lambda^3)V$ and each mode may contribute three vibrations (one longitudinal and two transverse). Thus the number of vibrations is $(4\pi/\lambda^3)V$.

n_3 being given by the relations $n_1 d = p$, $n_2 d = q$, $n_3 d = r$ if the interatomic distance is the same along the three principal directions. Slater[1] has discussed this fully and shows that on account of this the parabolic frequency distribution of Debye becomes modified in the region of ν_m, the curve instead of falling sharply at ν_m, begins to fall earlier and continues upto some distance beyond ν_m. Accurate calculation however requires a knowledge of the crystal structure.

16·20. Born's Theory of Vibration of Crystals.—Even with the modifications discussed above, the theory is inapplicable to anisotropic solids or crystals where the velocity of elastic waves varies with direction. We have also not taken into account the variation of velocity with wavelength. Born and Karman therefore worked out the equations of motion for the atoms of the solid, assuming that the atoms interact only with their neighbours and in accordance with Hooke's law. Assuming the "periodic" boundary conditions Born showed[2] that N atoms arranged in a three-dimensional crystal lattice would give the same vibrations as obtained by the continuum method; only we should calculate with the assumption of different ν_m for the different directions for each polarised wave since the velocity is different in different directions. If there are N molecules, each consisting of n atoms, Born postulated that only the $3N$ degrees of freedom which correspond to *intermolecular* vibrations, should be treated by the continuum method, the contribution of the remaining $3(n-1)$ sets of N frequencies corresponding to *intra-molecular* vibrations being given by $3(n-1)$ Einstein terms. With this assumption the specific heat of a gram-molecule is

$$C_v = R\sum_{j=1}^{j=3}\int_{\Omega} D\left(\frac{\Theta_j(\theta,\phi)}{T}\right)\frac{d\Omega}{4\pi} + R\sum_{i=1}^{3(n-1)} E\left(\frac{\Theta_i}{T}\right). \quad \quad (62)$$

For an isotropic medium this reduces to

$$C_v = R\sum_{j=1}^{3} D(\Theta_j/T) + R\sum_{i=1}^{3(n-1)} D(\Theta_i/T). \quad . \quad . \quad (63)$$

If the molecule is diatomic

$$C_v = R\left[\sum_{j=1}^{3} D(\Theta_j/T) + \sum_{j=4}^{6} E(\Theta_j/T)\right] \quad . \quad . \quad . \quad (64)$$

On this basis the specific heat of AgCl, NaCl etc. may be calculated.

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[1] Loc. cit.

[2] For details of deduction and an excellent review of the subject see Seitz, *The Modern Theory of Solids* (1940), Chap. III. See also Born and Goppert-Mayer, *Handbuch d. Physik*, Ed. 2, **24**, part II, p, 623 (1933); Born, Atomtheorie des festen Zustandes, *Encycl. Math. Wiss.* **5**, part 3 (1923).

Blackman[1] has extended Born's calculations by assuming interaction not only with the immediate neighbours but also with the next immediate neighbours. Blackman's calculations, are essentially qualitative but they seem to throw some light on the behaviour of specific heat at low temperatures.

The theories of Debye and Born have been applied quite generally to all substances and in some cases deviations have been observed. It is doubtful if Born's method of separating Debye and Einstein terms is justified for all ionic and molecular crystals. The observed deviations in some cases are due to the fact that Hooke's law is not obeyed and anharmonic interaction terms must be taken into account; this is so for high temperature deviations from Dulong and Petit's law. In some cases the contribution of electrons to the specific heat causes discrepancy; this is so at very low or very high temperatures. In some others, change in lattice structure is the cause of the anomaly. Examples of these will be found in the next section.

16·21. Importance of Investigations on Specific Heat.—The detailed investigation of the variation of specific heat with temperature is of great importance for a proper understanding of the condensed state of matter. In recent years such investigations are being carried out at many laboratories with great precision and care, and are sometimes yielding quite unexpected results. It is impossible to give a detailed description of all these results for which special treatises must be consulted but the more important ones are indicated below:—

Metals.—The general course of the specific heat of all metals is given by the Dulong-Petit law at ordinary temperatures viz. $C_v = 3\,R$, and by the Debye formula at lower temperatures. But whenever there is any important change in the physical properties, this is indicated usually by a discontinuity in the specific heat.

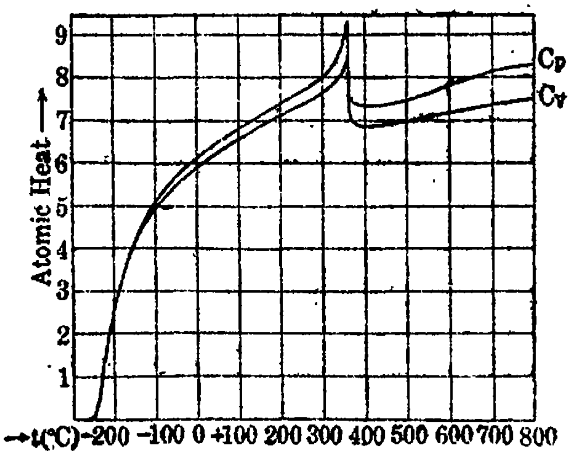

Fig. 13.—Atomic Heat of Nickel showing discontinuity at the Curie-point.

Discontinuity at the Curie Point.—A very good example is afforded by the ferromagnetic substances (iron, nickel, cobalt) which lose their "Ferromagnetism" at a certain temperature called the *Curie point* and pass to the paramagnetic state. The specific heat also drops suddenly as shown in Fig. 13. It is seen that C_v suddenly drops from 8·2 to 7 cal. at 358°C. Similar behaviour is also shown by Fe and Co. But after the point is passed, the curve runs smoothly in the Debye fashion.

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[1] *Proc. Roy. Soc.*, **148**, 365, 384, 1935; **159**, 416, 1937; **181**, 58, 1942

The abnormality of specific heat has been traced sometimes also to crystal structure. Metals are aggregates of small crystals, most of which have simple forms like face-centred, or body-centred cubes. The crystals generally have one atom to a unit cell, but some have two or more, such as Germanium, which follows a Debye-curve, but at 70°K, C_v jumps suddenly from $\simeq$3·6 to 5·1; and Hafnium whose C_v jumps at 60°K from 5·3 to 11·2 within small temperature ranges. Both of these contain 2 atoms per cell of their crystal.

Electronic Specific Heat.—All metals are distinguished by high electrical and thermal conductivity which are ascribed, as mentioned in §14·15, to the presence of free electrons. As shown there, according to the elementary theory of Drude and Lorentz, both these quantities depend on the value of $n\lambda$, where 'n' is the number of free electrons per unit volume, and λ is the mean free path. As the two quantities occur always as a product, it is difficult to calculate n and λ separately. If we assume n to be proportional to the number of atoms per c.c. as seems natural, we are faced on the classical theory of equipartition with the difficulty that the contribution of electrons to the total atomic heat has almost as large a value as that due to the atoms *i.e.*, the atomic specific heat of metals would be very nearly $\frac{9}{2}R$ instead of 3R as observed.

Sommerfeld[1] has however shown that the electrons inside the metal form a degenerate gas and do not follow Maxwell's statistics, but the newer F.D. statistics (Chap. XVII). Assuming that the number of free electrons is equal to the number of atoms it is shown in Chap. XVII, that the specific heat term due to free electrons is given by

$$C_{ve} = \frac{Nm}{h^2}(2\pi k)^2 \left(\frac{\pi}{3n}\right)^{2/3} T \quad . \quad . \quad . \quad . \quad (65)$$

This formula can be utilized to calculate the heat capacity due to free electrons in a metal like silver. We have from (65), putting m= electron mass, $C_{ve} = 0\cdot767\times10^{-4}\,RT$ per gm. atom. = 0·046 cal. per gm.-atom at 300°K. Thus C_{ve} forms only 0·7% of the ordinary specific heat of silver at 300°C, and hardly adds anything to it. This removes one of the difficulties of the electron theory of metals.

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[1] *Zeits. f. Physik,* **48**, 1, 1928.

But at low temperatures, the specific heat due to lattice vibrations diminishes according to the law βT^3 where $\beta = 77 \cdot 94 \times 3R/(217)^3 = 4 \cdot 55 \times 10^{-5}\, T^3$. This becomes small compared to the electronic specific heat of Ag from the temperature range 3°K downwards. Keesom and Kok measured the specific heat of silver in this range and found that from 1·5°K to 3°K, the specific heat varies according to (65), but above 3°, the T^3-term predominates. This appears to suggest that below 3°K for Ag, free electrons become the chief contributor to specific heat.

The specific heat of Nickel was investigated by Keesom and Clark in the liq. He region. They found that T^3-law held in the higher range with $\Theta = 464 \cdot 5$ (the elastic constants give $\Theta = 413$); deducting the Debye term, which became inappreciable at lower temperatures, the atomic heat in the lower range (1·10—9·22°K) was found to follow the law $C_{ve} = 0 \cdot 001744\ T$. This is however nearly 15 times larger than the theoretical term due to electronic specific heat viz. $1 \cdot 148 \times 10^{-4}\ T$.

A certain amount of difficulty still remains in the interpretation of these results. For monovalent elements like Cu, n, the number of free electrons per c.c. is taken to be equal to the number of atoms per c.c., but even in this case, it is found that the experimental value of C_{ve} is 1·47 times higher. This is usually explained by saying that the electron mass m has to be substituted by a fictitious mass m^*, due to complexities of internal potential field. For Cu, $m^*/m = 1 \cdot 47$. For Al, having the structure $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p$, the number of free electrons per atom may be taken either 1, (the $3p$-electron) or 3 (the $3s^2\, 3p$ electrons). The values of m^*/m are respectively 2·30, and 1·61. For transitional metals like Ni, where the d-shell is not closed, the problem is more complex, for we have a large number of electrons which have a chance

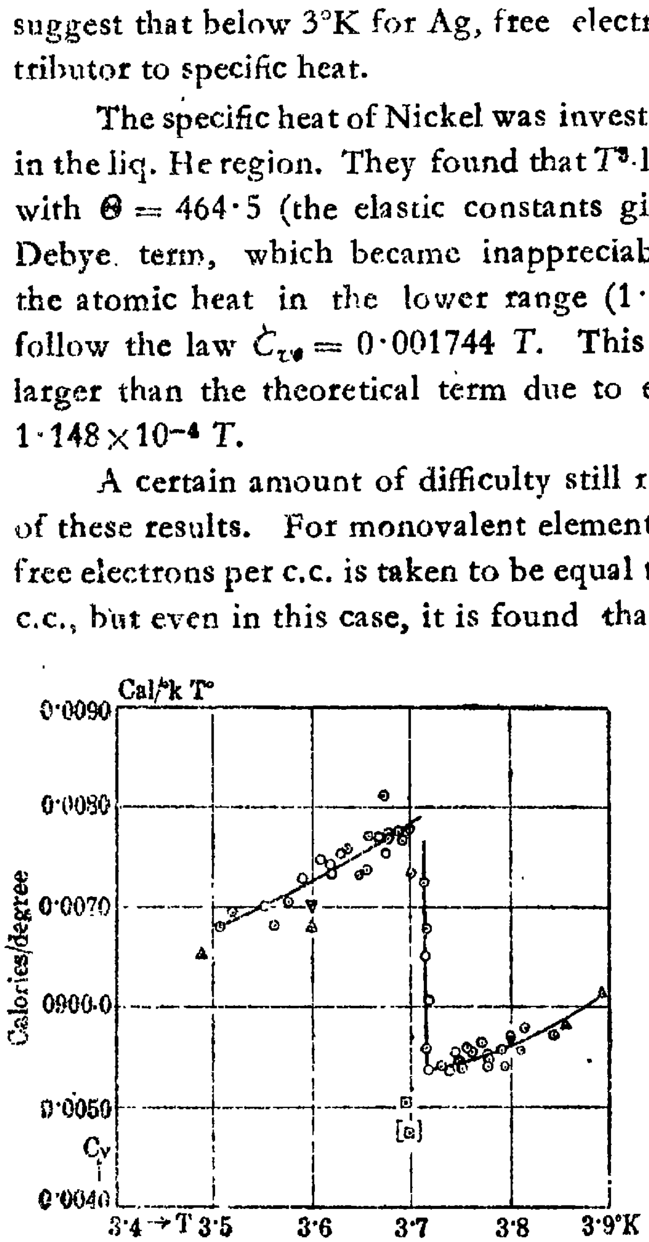

Fig. 14.—Atomic Heat of Tin. Note the sudden jump at $T = 3 \cdot 72$ where it becomes superconducting.

to be free. For Ni, we have the electronic constitution $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9\ 4s^1$, we have 9 electrons in the d-shell, and one in the s-shell. All of them have chances to be "free." In all such cases, m^*/m is found to be large as in the case of nickel. For further information, see Seitz, *loc. cit.*, Chap. IV.

Metals and alloys which show the phenomenon of superconductivity (§14·16), are also found to show an abrupt change in their specific heat at the same point, e.g. Keesom found that the atomic heat of tin changed from 0·0064 to 0·0078 cal./gm. exactly at the temperature of 3·72°K where it becomes superconducting. The superconducting temperature changes with the magnetic field and the specific heat is also found to change accordingly.

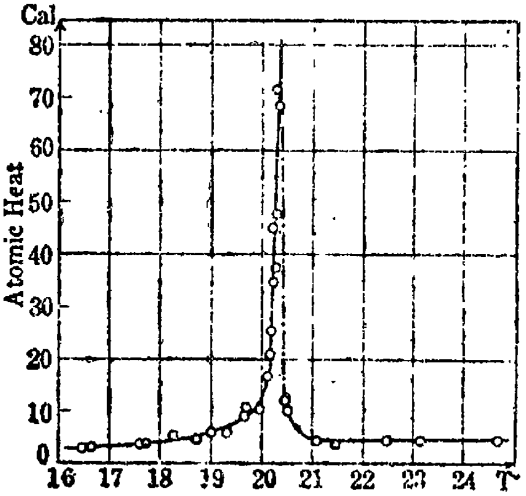

Fig. 15.—Variation of Atomic Heat C_p of solid Methane showing the sudden jump at 20·4°K.

Solid Methane.—A new type of discontinuity was first brought to light by Eucken, and has since been widely investigated by Simon, Giauque and others. The nature of this discontinuity is illustrated in Fig. 15, which shows the variation of specific heat of solid methane with temperature. The value suddenly shoots up at 20·4°K. On both sides of this point the curve is quite normal, say at $T < 17$°K and $T > 21$°K but between these two temperatures at 20·5°, the atomic heat shoots up about 13 times its normal value on the right side. Effect of this type was first discovered by Eucken for O_2(43·4°), N_2 and CO in 1916, but their importance was first emphasized by Simon who discovered the same discontinuity for NH_4Cl, HCl, HBr, HI (the last two show two such points), CH_4 (Clusius and Perlick) and liquid Helium (Keesom and Wolfke). According to Pauling, this temperature of jump marks an internal change in the nature of motion executed by the constituent particles. At the lower temperature, the molecules or ions constituting a crystal execute a rotatory motion round an axis perpendicular to the molecular axis which is however not complete, *i.e.*, the angle of rotation varies within certain limits. At the transition point, it suddenly changes to complete rotation. Frenkel, on the other hand, thinks that the molecules undergo only torsional oscillations both above and below the transition temperature and that they have less relative orientation above the transition than below it (see Lawson, *Phys. Rev.* **57**, 417).

16·22. Specific Heat of Liquids.—For liquids the value of C_v may be obtained either from the value of C_p or γ (determined directly by the velocity of sound method) by making use of the equation (20), p. 331. γ is found to vary rather widely with temperature in some cases. The difference $C_p - C_v$ is rather large for liquids. This is because $C_p - C_v = Ea^2Tv$ and the coefficient of expansion for a liquid is much larger than that for a solid. This point is illustrated in Table 11. The specific heat of metals varies slightly at the melting point while for non-metals the variation is rather large.

Table[1] 11.—*Molecular heats C_p and C_v in solid and liquid states.*

Substance	State of aggregation	C_p	C_v
H_2	Solid	1·4 (14°)	..
		3·3 (14°)	..
	Liquid	4·40 (20°)	2·8 (20°)
			3·2 (27°)
Ar	Solid	7·8 (78·3°)	5·66 (78·3°)
		10·50 (84·9°)	5·54 (88·4°)
		10·62 (93·9°)	5·50 (93·9°)
	Liquid	12·40 (123·8°)	5·10 (123·8°)
		15·41 (140·4°)	4·65 (140·4°)
Hg	Solid	6·8 (233°)	5·95 (233°)
		6·72 (273°)	5·97 (273°)
	Liquid	6·57 (373°)	5·45 (373°)
		6·62 (473°)	5·30 (473°)
K	Solid	7·81 (332°)	7·26 (332°)
	Liquid	7·96 (341°)	7·25 (341°)
Water	Solid	9·10 (273°)	9·0 (263°)
		18·100 (274°)	18·090 (274°)
	Liquid	18·015 (298°)	17·830 (298°)
		18·100 (330°)	17·650 (330°)

The value of C_v may be accounted for by the degrees of freedom of translation, rotation and vibration as in the case of gases (sec. 16·3). There is however no theory to explain quantitatively the observed variations of specific heat. The values of C_p are seen to vary widely, but those of C_v are found to be about 3R except for non-metals.

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[1] Taken from Eucken, *Lehrbuch der chemischen Physik*, p. 184.

PROBLEMS

1. Calculate the specific heat of carbon dioxide at constant volume at 1,000°C from the following data :—CO_2 has three fundamental vibration frequencies with wave numbers 1,388, 667·5 (double), and 2,350 cm^{-1}.

2. Calculate the specific heat at constant volume of aluminium at 100°K, given that the Debye temperature of aluminium is 396°K.

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CHAPTER XVII

THERMODYNAMICS OF QUANTUM-MECHANICAL SYSTEMS

17·1. Introduction.—It was explained in Chapter IX that the object of statistical thermodynamics is to find macroscopic properties of an assembly with the aid of a not-too-detailed microscopic analysis of the constituent particles (atoms, molecules, quanta and crystals) in thermal equilibrium and to discover what functions of their motions correspond to the macroscopic thermodynamical functions in their properties. In Chapter IX, however, we considered only a gaseous system consisting of spherically symmetrical, structureless particles of classical mechanics with very weak interaction. Actually however the molecules are made up of atoms, electrons, protons, neutrons, etc. and cannot in most cases, as we now know, be regarded as symmetrical. The internal degrees of freedom of the molecules must be taken into account and these are subject, not to classical, but to quantum-mechanical laws as we saw in Chapter XVI.

Even for spherically symmetrical particles we found in Chapter IX that the expression obtained for entropy by Boltzmann's method of counting was not correct and we had to divide arbitrarily the value of the thermodynamic probability by $N!$ in order to get the correct expression for entropy. No satisfactory reason can be given for this procedure of division by $N!$ from classical ideas. The reason is really a quantum-mechanical one and arises from the fact that the molecule cannot be regarded as a spherical mass-point, obeying classical dynamics, but it has to be represented by a ψ-function, obeying wave mechanics. The N-particles forming a system cannot be regarded as statistically independent as was implied in Boltzmann's way of counting since, on account of the Uncertainty Principle, these identical particles cannot be told apart, or when we consider collisions, it is not possible to identify the molecules after collisions. The effect of quantum mechanical considerations is, as shown in Note 15, that the Planck's expression for thermodynamic probability must be divided by $N!$ in case of structureless molecules. This new expression for probability we may call as effective statistical probability for the system. It was shown that

$$S = k \ ln \frac{P}{N!} + S_0 \quad . \quad . \quad . \quad . \quad (1)$$

where S_0 may be put equal to zero for spherically symmetrical molecules in conformity with Nernst Heat Theorem (§17·19).

It has already been pointed out in Chapter IX that two powerful methods have been developed for building up the science of statistical mechanics: one due to Gibbs and the other due to Fowler and Darwin. The adaptation of the former to the case of quantum-mechanical systems is not easy. The second method is easily adaptable to quantum-mechanical systems and is often used for studying complicated systems. It however requires a knowledge of complex variables and contour integration.[1] We shall therefore continue to adopt the simpler method based on the use of Stirling's theorem and content ourselves by merely calculating most probable values.

17·2.—Calculation of Statistical Probability and number of cells according to quantum-statistics.—The most satisfactory way to calculate statistical probability is from wave-mechanics. This is done in Note 15. But an easier approach first given by Einstein, which arose out of a work by S. N. Bose on the statistics of photons (§17·11), is followed here. This treatment applies only to the translational motion of structureless spherical particles, when the interaction amongst the particles is neglected altogether.

Let us, as in §9·4, consider particles which have energies[2] lying between ϵ_t and $\epsilon_t + d\epsilon_t$. The phase-volume at the disposal of each of these particles is equal to G_t given by the relation

$$G_t = \iiint dx.dy.dz \iiint dp_x \, dp_y \, dp_z. \quad . \quad . \quad (2)$$

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[1] This method appeals to some scholars as being more convincing. Its advantages, however, are that (1) it makes use of mean values instead of most probable values, (2) it is directly applicable to strongly interacting systems such as solids where interaction energies must also be taken into account. In this method the different states of the entire assembly, rather than of particles, is considered. The method developed in the following pages is applicable only to non-interacting or weakly interacting systems such as the molecules of a gas where we can talk of the private energies of the molecules.

[2] The subscript 't' denotes that we are dealing with translational motion.

the integration to be done within the energy-limits ϵ_t, $\epsilon_t + d\epsilon_t$. G_t is easily seen to be given by

$$G_t = 2\pi V(2m)^{3/2}\,\epsilon_t^{\frac{1}{2}}\,.\,d\epsilon_t, \quad . \quad . \quad . \quad . \quad (3)$$

for the first part of integral (2) is merely V, the volume occupied by the particles. The second integral is the element of volume included within the concentric spheres $p_x^2 + p_y^2 + p_z^2 = 2m\epsilon_t$, and $p_x^2 + p_y^2 + p_z^2 = 2m(\epsilon_t + d\epsilon_t)$. This is easily seen to be $2\pi\,(2m)^{3/2}\,\epsilon_t^{\frac{1}{2}}\,.\,d\epsilon_t$.

Now from the quantum theory, we know that for each degree of freedom, a particle has the phase-space $\int\int dp.dq = h$. Hence for the three degrees of freedom, which particles composing a monatomic gas possess, the phase integral $\int \ldots \int \Pi\, dp.dq$ amounts to h^3. We might therefore say that the volume of phase space occupied by each particle is h^3. This can be taken to be the volume of an elementary cell of the phase-space. Hence the number of cells a_t at the disposal of the particles of energy between ϵ_t and $\epsilon_t + d\epsilon_t$ is given by

$$a_t = \frac{2\pi V(2m)^{3/2}\epsilon_t^{\frac{1}{2}}\,d\epsilon_t}{h^3} \quad . \quad . \quad . \quad . \quad (4)$$

Now according to §9·4, equation (12), n_t is the number of particles which are to be accommodated in these cells. Let us now find out the number of ways P_t in which this can be done.

17·3. Bose-Einstein, Fermi-Dirac and Classical Statistics.—There are three ways of calculating the probability P_t depending upon the statistics the particles obey :—(a) Bose-Einstein, (b) Fermi-Dirac, (c) Classical. Let us consider the three methods one after another. The particles are all indistinguishable from each other.

Case (a) : Calculation of P_t according to the Bose-Einstein statistics.

We have a_t cells and we have to place n_t particles in them. The question arises as to whether we can place in each cell one particle, or more than one. In the first instance we can suppose, as Einstein did, that there is no limit to the number of particles which a cell can contain; it can have any number from 0, 1, 2 upto n_t. The number of ways of accommodating n_t particles in a_t cells according to this conception is the old algebraic problem of combination with repetition. It is shown in Note 13 that this can be done in P_t -ways, where

$$P_t = \frac{(a_t+n_t-1)\,!}{(a_t-1)\,!\;n_t\,!} \simeq \frac{(a_t+n_t)\,!}{a_t\,!\;n_t!}. \quad . \quad . \quad . \quad (5)$$

We have therefore

$$P_T = \prod P_t = \prod_t \frac{(a_t+n_t)!}{a_t\,!\;n_t!} \quad . \quad . \quad . \quad . \quad (6)$$

where the product extends over all the energy-layers ϵ_t.

Case (b) : Probability from Fermi-Dirac Statistics.

In this statistics it is assumed that a particular cell cannot contain more than one particle. The problem is now distribution of n_t particles amongst a_t cells, so that a cell contains not more than one particle. The number of ways P_t of doing so is given by ordinary algebra to be the expression for combination without repetition, viz.

$$P_t = \frac{a_t\,!}{(a_t-n_t)\,!\;n_t\,!}. \quad . \quad . \quad . \quad . \quad (7)$$

so that we have

$$P_T = \prod P_t = \prod_t \frac{a_t\,!}{(a_t-n_t)\,!\;n_t\,!} \quad . \quad . \quad . \quad . \quad (8)$$

Case (c) : Classical Case.

When $a_t \gg n_t$, as is usually the case, it can be easily verified that both B-E and F-D expressions (5) and (7) reduce to the form

$$P_t = a_t^{n_t}/n_t\,! \quad . \quad . \quad . \quad . \quad . \quad (9)$$

so that

$$P_T = \prod_t a_t^{n_t}/n_t\,! \quad . \quad . \quad . \quad . \quad (10)$$

N. B. Apply Stirling's Theorem, as given in Note 7.

This is the Classical Statistics, which can be deduced in a number of other ways, not always satisfactory.[1]

17·4. Distribution Law according to the Three Statistics.—We shall now work out the equilibrium conditions from the three statistics, and deduce expressions for distribution functions. We have

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[1] First, we have N distinct particles and we have to choose groups of $n_0, n_1, \ldots n_t$ from the whole. This can be done in $N!/\prod n_t!$ ways. Secondly, we have to distribute n_t particles amongst the a_t cells, each cell being capable of accommodating 0, 1, 2. . . . upto n_t particles. The first particle can be accommodated in a_t ways, either in the 1st, 2nd or a_t-th cell and for these, the second can also be accommodated in a_t

I. Classical	II^a. B-E	II^b. F-D
$P = \prod \frac{a_t^{n_t}}{n_t!}$	$P = \prod \frac{(a_t+n_t)!}{a_t!\, n_t!}$	$P = \prod \frac{a_t!}{(a_t-n_t)!\, n_t!}$

Let us now calculate S from the relation $S = k\, ln\, P$ using Stirling's theorem (Note 7). We obtain after some work

$$\left.\begin{array}{lll} \text{I. Classical}: & S/k = \sum n_t \,.\, ln\,(a_t/n_t) + N \\ \text{II}^a\text{. B-E} & : S/k = \sum [n_t\, ln\,\{(a_t+n_t)/n_t\} + a_t \,.\, ln\,\{(a_t+n_t)/a_t\}] \\ \text{II}^b\text{. F-D} & : S/k = \sum [n_t \,.\, ln\,\{(a_t-n_t)/n_t\} - a_t \,.\, ln\,\{(a_t-n_t)/a_t\}] \end{array}\right\} \quad (11)$$

II^a and II^b can be combined under the single form :

$$\text{II.} \quad S/k = \sum [\{n_t \,.\, ln\,\{(a_t+\gamma n_t)/n_t\} + \gamma a_t\, ln\{(a_t+\gamma n_t)/a_t\}]. \quad . \quad (12)$$

If we put $\gamma = 1$, we get BE-statistics; $\gamma = -1$ gives us FD-statistics. Putting $\gamma = 0$, we get classical statistics for N in 11(I) can be neglected.

The equilibrium state is obtained from the conditions :

$$\delta S = 0, \quad \delta N = \sum \delta n_t = 0, \quad \delta U = \sum \epsilon_t . \delta n_t = 0 \quad . \quad . \quad (13)$$

Using the first of these conditions, and remembering that a_t does not vary, we deduce from (11) and (12) that

$$\text{I.} \quad \sum \delta n_t \,\{ln\,(a_t/n_t) - 1\} = 0, \qquad \text{II.} \quad \sum \delta n_t \,.\, ln\,\{(a_t+\gamma n_t)/n_t\} = 0. \quad . \quad (14)$$

Now using the method of undetermined multipliers we have from (13) and (14)

$$\left.\begin{array}{ll} \text{I.} \quad ln\,(a_t/n_t) - \alpha - \beta\epsilon_t = 0, & \text{or} \quad n_t = \frac{1}{f} a_t\, e^{-\beta\epsilon_t} \\ \text{II.} \quad ln\,\{(a_t+\gamma n_t)/n_t\} - \alpha - \beta\epsilon_t = 0, & \text{or} \quad n_t = \frac{a_t}{f e^{\beta\epsilon_t} - \gamma}. \end{array}\right\} \quad . \quad . \quad (15)$$

---

ways. For if the first particle is in the 3rd cell, there is no bar for the second also to be in the same cell. Proceeding in this way, we find that the n_t particles can be put into a_t-cells in $a_t^{n_t}$-ways. Thus we can effect the desired distribution in W_t different ways where W_t is given by

$$W_t = N! \prod \frac{a_t^{n_t}}{n_t!}.$$

This may be said to be the thermodynamical probability for the contemplated distribution. To obtain P_t we have to divide it by W_0 which is the number of ways in which the particles can be distributed amongst themselves when at rest. This is $N!$. P_t is obtained by dividing W_t by W_0 and is given by

$$P_t = \prod a_t^{n_t}/n_t!$$

where $f = e^{\alpha}$ is an unknown parameter to be called hereafter the "*Degeneracy Parameter*", whose value has to be inferred from the conditions of the case.

We notice that if $f \gg 1$ (weakly degenerate case) both B.E. and F.D-distributions reduce to case I (the classical case).

Value of β.—From (12) and (15), we have

$$\delta S/k = \sum \delta n_t \, . \, ln \, \{(a_t + \gamma n_t)/n_t\} = \sum \delta n_t \, (\alpha + \beta \epsilon_t)$$

$$= \sum \beta \delta n_t \, . \, \epsilon_t = \beta \, . \, \delta U.$$

Hence using the relation $\partial S/\partial U = 1/T$, we have $\beta = 1/kT$ for all statistics.

17·5. Law of Distribution in Classical Statistics.—Let us put

$$2\pi V.(2m)^{3/2}/h^3 = C. \quad . \quad . \quad . \quad (16)$$

We have $N = \sum n_t$ and $U = \sum n_t \epsilon_t$. Now replacing summation by integration and putting $\beta \epsilon_t = u$, we have from (4) and (15)

$$\left.\begin{aligned} N \, . \, f &= C\beta^{-3/2} \int_0^\infty e^{-u} . \, u^{1/2} . \, du = C\beta^{-3/2} . \, \Gamma(3/2), \\ U \, . \, f &= C\beta^{-5/2} \int_0^\infty e^{-u} . \, u^{3/2} . \, du = C\beta^{-5/2} \, \Gamma(5/2), \end{aligned}\right\} \quad . \quad (17)$$

where $\Gamma(n)$ is the Eulerian gamma-function

We have from (17), $U/N = \frac{3}{2}/\beta = \frac{3}{2}kT$ as we have obtained in §9·10. Further from (17^a) and (16) we have

$$f = C\beta^{-3/2} \, \Gamma(3/2)/N = \frac{(2\pi mkT)^{3/2}}{nh^3}, \quad . \quad . \quad . \quad (18)$$

where $n = N/V$ = number of particles per unit volume. We shall denote the value of f given by (18) as f_0.

Substituting this value of f in (15^a), we get for the number of particles having their energy between ϵ_t and $\epsilon_t + \delta \epsilon_t$,

$$n_t = 4\pi . N \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{1}{2}\frac{mc^2}{kT}} . \, c^2 . \, dc.$$

since $\epsilon = \frac{1}{2}mc^2$. This agrees with the expression already deduced (§3·18, formula (30)) for Maxwellian distribution.

17·6. Value of Entropy and other Thermodynamical Functions in B-E and F-D-statistics.—Using the same notation as in the previous paragraph, we have from (15^b),

$$Nf = C\beta^{-3/2}. \int_0^\infty \frac{u^{1/2}}{e^u - \gamma/f}\, du, \quad Uf = C\beta^{-5/2} \int_0^\infty \frac{u^{3/2}}{e^u - \gamma/f}\, du. \qquad (19)$$

Let us now introduce two integrals

$$I_{3/2} = \frac{1}{\Gamma(5/2)} \int \frac{u^{3/2}.\, du}{e^u - \gamma/f}, \quad \text{and} \quad I_{1/2} = \frac{1}{\Gamma(3/2)} \int \frac{u^{1/2}.\, du}{e^u - \gamma/f}. \qquad (20)$$

The general method of evaluating these integrals is given in Note 14. We have now

$$Nf = C\beta^{-3/2}\, \Gamma(3/2).I_{1/2}, \qquad Uf = C\beta^{-5/2}\Gamma(5/2).I_{3/2}. \qquad . \ (21)$$

Hence we have, after replacing β by its value $1/kT$,

$$U/N = \tfrac{3}{2}kT.\ I_{3/2}/I_{1/2} \quad . \quad . \quad . \quad . \quad . \ (22)$$

The value of pressure can be easily calculated from its expression in the kinetic theory of gases. We have for a perfect gas

$$p = \tfrac{1}{3}\Sigma m n_t v_t^2 = \tfrac{2}{3}\Sigma\, n_t.\ \epsilon_t = \tfrac{2}{3}.U/V, \quad . \quad . \quad . \ (23)$$

so that $pV = \frac{2}{3}U$ in all statistics.

Entropy.—We see from (11), with the help of (15), that for classical statistics

$$\begin{aligned} S &= k\Sigma\, n_t\, (\beta\epsilon_t + 1 + ln f) \\ &= \frac{U}{T} + \mathrm{R} + \mathrm{R}\, ln f = \frac{5}{3}\ \frac{U}{T} + \mathrm{R}\ ln\, f. \qquad . \quad . \ (24) \\ &= \mathrm{R}\ ln \frac{(2\pi mkT)^{3/2}\, e^{5/2}}{nh^3}. \quad . \quad . \quad . \quad . \quad . \quad . \ (25) \end{aligned}$$

from (17) and (18). This was already deduced in §11·21 and experimentally verified in §11·22.

As regards the other statistics, we have to start from (12). This gives us, with the help of (15^b),

$$S = \frac{U}{T} + \mathrm{R}\, ln f - k\gamma \sum a_t\, ln \left(1 - \frac{\gamma}{f}.\, e^{-\beta\epsilon_t}\right).$$

This last term can be replaced by an integral J, given by

$$J = -k\gamma \,.\, C \int_0^\infty \epsilon_t{}^{1/2} .\, ln \left(1 - \frac{\gamma}{f} .\, e^{-\beta\epsilon_t}\right) .\, d\epsilon_t$$

$$= -k\gamma .\, C\,(kT)^{3/2} .\, \int_0^\infty u^{1/2} .\, ln\,(1-\gamma e^{-u}/f) .\, du.$$

By partial integration, we find that

$$J = 2\pi V \frac{k(2mkT)^{3/2}}{h^3 f} .\, \gamma^2 \,.\, \tfrac{2}{3} .\, \int_0^\infty \frac{u^{3/2} .\, du}{e^u - \gamma/f} .$$

Hence remembering that in both BE- and FD-statistics, $\gamma^2 = 1$, we have the last term $= 2U/3T$. Hence, we have for a perfect gas

$$S = \frac{5}{3} \frac{U}{T} + \mathrm{R}\; ln\, f,$$

the same expression (24) as in classical statistics.

We now easily deduce the other thermodynamical functions.

$$\left.\begin{array}{llll} \text{The Free Energy :} & F = U - TS & = -\mathrm{R}T . ln\, f - \dfrac{2U}{3} \\ \text{The Gibbs' Potential :} & G = U + pV - TS & = -\mathrm{R}T .\, ln\, f \\ \text{The ThD. Potential :} & \psi = -G/T & = \mathrm{R}\; ln\, f. \end{array}\right\} . \quad .(26)$$

17·7. Statistics for weakly degenerate systems.—These are given by $f \gg 1$. We have from Note 14, for

$$\left.\begin{array}{l} \text{BE-statistics : } I_n = 1 + \dfrac{1}{2^{n+1}} . \dfrac{1}{f} + \dfrac{1}{3^{n+1}} . \dfrac{1}{f^2} \cdots + \dfrac{1}{(r+1)^{n+1}} . \dfrac{1}{f^r} \\ \text{FD-statistics : } I_n = 1 - \dfrac{1}{2^{n+1}} . \dfrac{1}{f} + \dfrac{1}{3^{n+1}} . \dfrac{1}{f^2} \cdots + (-1)^r \dfrac{1}{(r+1)^{n+1}} \dfrac{1}{f^r} \end{array}\right\} . \,(27)$$

If we retain only the first terms, we have $I_{3/2} = I_{1/2} = 1$, and from (22), $U = \frac{3}{2} NkT$, $pV = NkT$, as in classical thermodynamics.

Let us now proceed to a second approximation. We have from (21^a), using (16) and (27),

$$\frac{nh^3}{(2\pi mkT)^{3/2}} = \frac{1}{f_0} = \frac{1}{f} \pm \frac{1}{2^{3/2}} . \frac{1}{f^2} + \ldots ,$$

or

$$\frac{1}{f} = \frac{1}{f_0} \mp \frac{1}{2^{3/2}} . \frac{1}{f_0{}^2} . \quad . \quad . \quad . \quad (28)$$

approx. Substituting the value of $I_{3/2}/I_{1/2}$ from (27) in (22) and further using (28), we have

$$U = \frac{3}{2} RT\left(1 \mp \frac{1}{2^{5/2}} \cdot \frac{1}{f_0}\right) = \frac{3}{2} RT\left(1 \mp \frac{\cdot 176}{f_0}\right) \quad . \quad . \quad (29)$$

and from (23)

$$p = \frac{2}{3}\frac{U}{V} = \frac{RT}{V}\left(1 \mp \frac{\cdot 176}{f_0}\right). \quad . \quad . \quad . \quad . \quad (30)$$

The upper sign refers to BE, and the lower sign to FD-statistics.

From (25), using (29) and (28), we easily observe that for

$$\left.\begin{array}{l} \text{B.E.-Statistics}: S = \frac{5}{2}R + R\, ln\, f_0 - \cdot 088\ R/f_0 \\ \text{F.D.-Statistics}: S = \frac{5}{2}R + R\, ln\, f_0 + \cdot 088\ R/f_0 \end{array}\right\} \quad . \quad . \quad (31)$$

17·8. Experimental tests of new statistics for weakly degenerate systems.—Let us now see if it is possible to put these results to experimental test.

We must choose for this purpose a gas under such physical conditions that the degeneracy parameter

$$f_0 = \frac{(2\pi mkT)^{3/2}}{nh^3} = \frac{(2\pi m)^{3/2}\, k^{5/2}}{h^3} \cdot \frac{T^{5/2}}{p}$$

is as small as possible, consistent with the system being weakly degenerate, so that the second term in (30) is appreciable. This objective is achieved only when the substance has small molecular weight and large vapour pressure at small values of temperature. Calculation shows helium alone of all elements to satisfy these conditions. We have for helium

$$f_0 = 2 \cdot 4 \times 10^5 \,.\, T^{5/2}/p. \quad . \quad . \quad . \quad . \quad . \quad (32)$$

The saturated vapour pressure of He, as obtained from the measurements of the Leiden school, are given[1] in column 2 of Table 1. From these, the values of f_0 are calculated in column 3. At 4·240°K, the value of f_0 is 8·64, so that $pV = RT(1 - \cdot 02)$ i.e., the deviation from the law of perfect gases due to BE-degeneracy is expected to be only 2 % at the boiling point of helium.

The equation of state of the vapour is represented by a Kammerlingh Onnes type of equation:

$$pV = RT\left\{1 + \frac{B(T)}{V}\right\} \quad . \quad . \quad . \quad (33)$$

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[1] See *Helium* by Keesom, p. 189. For *B*-values see p. 49 of the same book.

The second term $B(T)/V$, has the same form as the deviation due to BE-degeneracy viz. $\cdot 176/f_0$, for $1/f_0 \propto n \propto 1/V$. The experimental values of $B(T)$ are shown in column (4), and the values calculated from BE-degeneracy in column (5). It is seen that they do not agree. But Beth and Uhlenbeck (*Physica*, **4**, 915, 1937) have shown that the van der Waals terms also contribute to the B-term in the same direction as the BE-degeneracy. Their values are given in column (6) and the two together given in column (7) almost completely account for the experimental values of B as given in column 4. The work appears to establish the reality of the BE-degeneration, though not in a very convincing manner[1].

Table 1.—*Second Virial Coefficient for Helium.*

T°K	p in cm of Hg.	f_0	B (Exp.)	B (B-E)	B (van d. Waals)	B (Theo.)
4·240	77·6	8·64	—75·7	— 8	—60·8	—68·8
3·723	46·2	10·5	—87·8	— 9·8	—70·2	—80
3·105	21·3	14·4	—107	—12·8	—86·0	—98·8
2·647	10·2	20·1	—128	—16	—104	—120
2·050	2·8	38·7	—180	—25	—142	—167

7·9. Strongly Degenerate Fermi-Dirac Systems.—But though for ordinary gases, f_0 is generally found to be >1, it may not be so for the electron gas, for in this case the mass is 1/1836-times the mass of the H-atom, and a glance at (18) shows that f_0 may be $\ll 1$.

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[1] Ordinary helium gas contains an isotope He^3 in the extremely small proportion of $10^{-7} : 1$. It was considered next to impossible to isolate it in sufficient quantity for experimental purposes by any physical method. But H^3 or tritium grows by β-decay to He^3, and taking advantage of this fact, sufficient quantities of He^3 were grown at the Los Alamos Atomic Energy Laboratory out of aqueous solutions in which the hydrogen of the water was replaced by pure tritium. The vapour pressure of He^3 has been determined from 1·2°K ($p=23$ mm) to 3·2°K ($p=760$ mm). The value of f_0 at the boiling point of He^3 comes out to be 2·66, so that if He^3 obeys FD-statistics, p should be equal to $\frac{RT}{V}\left(1+\frac{\cdot 176}{2\cdot 60}\right)$ i.e., nearly 7% higher than the theoretical value. The data, as yet, are too meagre for a satisfactory comparison. More recently properties of mixtures of He^3 and He^4 have been investigated extensively.

But in nature, it is not possible to have an atmosphere of pure electron gas, as it would dissipate to nothing on account of electrostatic repulsion. But as mentioned in §14·16, Drude and Lorentz showed that the electrical conductivity of a metal may be explained as being due to the motion of electrons, which exist as a free gas in the interstices of the crystal-lattice forming the metal. Sommerfeld then showed that these electrons form a degenerate gas, for putting proper values

$$f_0 = (2\pi mkT)^{3/2}/nh^3 = 2\times 10^{15}\, T^{3/2}/n.$$

If we now suppose that the number of free electrons is equal to the number of atoms per c.c. i.e. $n \simeq 10^{22}$, we find that even for ordinary temperatures viz. $T=300°$ K, $f_0 \simeq 10^{-3}$. These and other reasons make it necessary for us to give deductions for the case when $f \ll 1$.

For a BE-gas, however, f cannot be <1, for a glance at the distribution formula $n_t = a_t/(fe^{\beta\epsilon_t}-1)$ shows that if $f<1$, then for $\epsilon_t=0$, n_t comes out to be negative which is physically absurd. Hence for BE-gas, the lowest value of f is unity. A possible application is given in §17·10. $f<1$ applies only to FD-gas.

In this case, according to Note 14, we have, putting $ln\, f = -\alpha$,

$$\left.\begin{aligned} I_{3/2} &= \frac{8}{15\sqrt{\pi}} f\alpha^{5/2}\left(1+\frac{5\pi^2}{8\alpha^2}+\dots\right) \\ I_{1/2} &= \frac{4}{3\sqrt{\pi}} f\alpha^{3/2}\left(1+\frac{\pi^2}{8\alpha^2}+\dots\right) \end{aligned}\right\} \quad . \quad . \quad . \quad (34)$$

From (21) we obtain, using (34),

$$N = \frac{V}{h^3}\cdot\frac{4\pi}{3}(2mkT)^{3/2}\,\alpha^{3/2}\left(1+\frac{\pi^2}{8\alpha^2}+\dots\right) \quad . \quad (35)$$

Let the first-approximation value of α be α_0. Then we have

$$\alpha_0 = \left(\frac{3n}{4\pi}\right)^{2/3}\frac{h^2}{2mkT}. \quad . \quad . \quad . \quad . \quad (36)$$

Now (35) takes the form

$$\alpha_0{}^{3/2} = \alpha^{3/2}\left(1+\frac{\pi^2}{8\alpha^2}+\dots\right),$$

from which we deduce that to a second approximation

$$a = a_0\left(1 - \frac{\pi^2}{12a_0^2}\right). \qquad \ldots \ldots \qquad (37)$$

Now from (22), using (34), we obtain

$$\frac{U}{RT} = \frac{3}{5}a_0\left(1 + \frac{5\pi^2}{12a_0^2}\right),$$

or, writing in full,

$$U = \frac{3}{40}\cdot\frac{Nh^2}{m}\left(\frac{6n}{\pi}\right)^{2/3} + \tfrac{1}{2}\cdot\frac{Nm}{h^2}(2\pi k)^2\left(\frac{\pi}{6n}\right)^{2/3} T^2 \quad . \quad (38)$$

The expression shows that even at $T = 0$, the energy of an FD-gas satisfying the condition $f \ll 1$, is not zero, but has a finite value[1]

$$U_0 = \frac{3}{40}\,\frac{Nh^2}{m}\left(\frac{6n}{\pi}\right)^{2/3} \qquad \ldots \ldots \qquad (38')$$

This may be called the null-point energy.

The energy U adds a term to the specific heat given by $C_v = dU/dT = \gamma T$, where

$$\gamma = \frac{Nm}{h^2}(2\pi k)^2.\left(\frac{\pi}{6n}\right)^{2/3} \qquad \ldots \ldots \qquad (39)$$

In case of the electron on account of the spin (§17·12), the number of electrons, in any energy state will be twice that given by (15). The easiest way to take this into account is to replace V by $2V$ in all the formulae. Equation (39) therefore yields

$$C_{ve} = \frac{Nm}{h^2}(2\pi k)^2\left(\frac{\pi}{3n}\right)^{2/3} T. \qquad \ldots \qquad (40)$$

Application of (40) to the case of specific heat of metals at low temperatures has already been given in Chap. XVI, p. 739.

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[1] The expression for null-point energy and pressure can be easily derived from the following considerations:—The total phase volume occupied by N-particles at the A. N. is Nh^3, and hence the volume of the momentum sphere is $Nh^3/V = nh^3$. Putting this equal to $4\pi R^3/3$, where R is the radius of the momentum sphere, we have $R = (3n/4\pi)^{1/3}h$. We have therefore

$$\begin{aligned} U_0 &= \iiint \frac{\epsilon\,.\,dx\,.\,dy\,.\,dz\,.\,dp_x\,.\,dp_y\,.\,dp_z}{h^3} \\ &= \int_0^R \frac{p^2}{2mh^3}\,V.\,4\pi p^2 dp = \frac{2\pi V}{5mh^3}R^5 \\ &= \frac{3}{40}\cdot\frac{Nh^2}{m}\left(\frac{6n}{\pi}\right)^{2/3}. \end{aligned}$$

and

$$p = \frac{2}{3}\cdot\frac{U_0}{V} = \frac{1}{20}\,\frac{Nh^2}{Vm}\left(\frac{6n}{\pi}\right)^{2/3}$$

17·10. Limiting Case of BE-statistics and its application to the problem of Liquid He II.—The limiting case of BE-statistics referred to in the previous section (17·9) has received very ingenious application in the hands of Einstein, the brothers F. and H. London, Tisza and others for explaining the strange properties of Liq. He II (§12·29).

Supposing we can have a BE-gas for which the limiting value $f=1$ is reached, we have then from[1] (21) and (27), the following value of limiting particle density:

$$n = \frac{N}{V} = \frac{(2\pi mk)^{3/2}}{h^3} T^{3/2} I_{1/2}(1). \quad . \quad . \quad . \quad (41)$$

The value of $I_{1/2}(1) = 2 \cdot 612$. Applying the constant proper to the λ-point of He viz. $V=27 \cdot 4$ c.c. for a gm-molecule of He in the liquid state, we find that the temperature at which this takes place is given by

$$T = \left(\frac{N}{2 \cdot 612\, V}\right)^{2/3} \cdot \frac{h^2}{2\pi mk} \simeq 3 \cdot 12^\circ\text{K} \quad . \quad . \quad (42)$$

for He. This is not far removed from the observed temperature[2] of the λ-point, viz. 2·18°K.

F. London argues that the transition Liq. He I to Liq. He II marks the stage where the limiting value $f=1$ for a BE-system is reached and some proportion of He-atoms start reaching the zero-energy state. If we try to raise the value of f, by further cooling, this results in a fresh number of atoms of He passing to the zero-energy state. Liq. He II can thus be considered as a mixture of two interpenetrating liquids, one consisting of atoms of zero energy and zero entropy, and possessing, as we shall see (Note 17), the properties of *superfluidity*, and the other an ordinary liquid. At the λ-point, the *superfluid* just begins to be formed, and goes on increasing in relative proportion as the temperature is lowered and at the absolute zero the whole mass is a superfluid.

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[1] In assuming (21) to hold right to the zero energy state we necessarily make the assumption that the statistical weight of the lowest state $\epsilon=0$ is zero (since $u=0$) instead of unity as it should be. This can be easily corrected for by adding the term $1/(f-1)$ in (21) which is the number of particles in the zero state from (15).

[2] See Chapter XII.

It can be seen that the argument is a bit strained for formula (41) holds for a gaseous assembly for which the interaction between particles is completely disregarded, whereas it is here applied to the case of matter in a liquid[1] state of aggregation, for which the interaction is important. It is however known that liquid helium has a high zero-point energy which forces the particles far apart; it is therefore no wonder that the gas approximation for liquid helium is not so inadequate as one might think. Further attempts have been made by several workers by considering liquid helium as a Bose-Einstein liquid but it is now more usual to construct a quantum theory of liquid helium by direct quantization of hydrodynamical variables such as the density, the current and the velocity without explicit reference to the interatomic forces. For fuller information see R. B. Dingle, *Advances in Physics* Vol. 1, p. 111 (1952).

17·11. Statistics of Photons, and Bose's deduction of Planck's Law.—In §15·32 it was mentioned that a black-body chamber may be supposed to be full of photons in thermal equilibrium. The problem of finding the spectral distribution of energy (intensity of ν-radiation) then reduces to that of finding the number of photons possessing the energy $h\nu$ in a black-body chamber having the temperature T. The problem was conceived in this way first by S. N. Bose who gave a very elegant method for its solution.

We already mentioned that according to the quantum hypothesis the ν-radiation consists of photons having the energy-content $h\nu$ and moving in any possible direction with the constant velocity 'c', and therefore possessing the momentum $h\nu/c$. The photon is therefore just like a particle with $(p_x, p_y, p_z) = \frac{1}{c}(h\nu_x, h\nu_y, h\nu_z)$ where $(\nu_x, \nu_y; \nu_z) = \nu(\alpha, \beta, \gamma)$, α, β, γ being the direction cosines of the direction of motion of the photon. We have

$$p_x^2+p_y^2+p_z^2=h^2\nu^2/c^2. \qquad . \quad . \quad . \quad . \quad (43)$$

Let us now find out the phase volume described by the photons within the energy layers $h\nu_s$ and $h(\nu_s+d\nu_s)$. This is given by

$$G_s = \int \cdots \int dx\,dy\,dz.\ dp_1 dp_2 dp_3 = V.\ \frac{4\pi\nu_s^2\, d\nu_s}{c^3}.\ h^3 \quad . \quad . \quad (44)$$

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[1] It has been shown experimentally that the rare isotope He^3 which obeys F. D.-statistics has neither a lambda point nor shows superfluid properties down to 0·25°K. This suggests that the behaviour of He^4 is to be correlated with the fact that it obeys B.E.-statistics. Properties of mixtures of He^4 and He^3 have therefore been extensively investigated in recent years for elucidating these phenomena. For details see Daunt and Smith, *Rev. Mod. Phys.* **26**, 172 (1954).

since $p_1^2+p_2^2+p_3^2=h^2\nu_s^2/c^2$, and we are integrating within the limits $\nu_s+d\nu_s$ and ν_s.

This is the phase-volume at the disposal of the photons lying within the energy layers $h\nu_s$ and $h(\nu_s+d\nu_s)$. But each photon has the phase-volume h^3. Hence the number of cells per unit volume

$$A_s d\nu_s = \frac{G_s}{h^3} = \frac{4\pi\nu_s^2 d\nu_s}{c^3}.$$

The number has to be doubled because to a definite frequency and direction, there are two photons distinguished by their state of polarisation from each other. Therefore the total number of cells or degrees of freedom of the ν_s-quanta is given by

$$A_s d\nu_s = \frac{8\pi\nu_s^2 d\nu_s}{c^3} \quad . \quad . \quad . \quad . \quad . \quad (45)$$

The quantity $A_s d\nu_s$ is seen to be identical with the number of waves in a cubical enclosure having their frequencies between ν_s and $\nu_s+d\nu_s$ as proved on p. 666. Thus Bose's method simplifies to a remarkable extent the complicated mathematics used in §15·28 for the deduction of this result.

Let the number of photons of frequency between ν_s and $\nu_s+d\nu_s$ be denoted by $N_s\,d\nu_s$. We have then to find out the number of ways in which the $N_s d\nu_s$ oscillators can be distributed amongst the $A_s\,d\nu_s$ cells. We make the supposition that each cell may contain 1, 2, 3,. . r. . up to $N_s\,d\nu_s$ photons. Then we get

$$P = \prod \frac{(A_s+N_s)\,d\nu_s\,!}{A_s d\nu_s\,!\,N_s d\nu_s\,!}, \quad . \quad . \quad . \quad . \quad (46)$$

as explained on p. 747. We have, using Stirling's approximate formula,

$$S = k\,ln\,P = k\sum d\nu_s\,ln\,\frac{(A_s+N_s)\,!}{A_s\,!\;N_s\,!}.$$

To obtain the law of distribution we make $\delta S=0$, subject to the condition

$$E = \Sigma\,(N_s\,d\nu_s)\,h\nu_s = \text{constant}.$$

We have therefore

$$\delta\;\Sigma\;[(A_s+N_s)\,ln\,(A_s+N_s)-N_s\,ln\,N_s-A_s\,ln\,A_s] = 0,$$

subject to the condition

$$\Sigma\,\nu_s\;\delta N_s = 0.$$

Using an undetermined multiplier, the conditions yield

$$ln\,(A_s+N_s)-ln\;N_s-a\nu_s = 0,$$

or

$$\frac{A_s+N_s}{N_s} = e^{a\nu_s}, \quad \text{or } N_s = \frac{A_s}{e^{a\nu_s}-1}. \quad . \quad . \quad . \quad (47)$$

From the condition $\partial S/\partial E = 1/T$, we obtain $\alpha = h/kT$. We have therefore[1]

$$N_s = \frac{A_s}{e^{h\nu/kT}-1} \quad . \quad . \quad . \quad . \quad . \qquad (48)$$

Now the energy density $= \rho_{\nu_s}\, d\nu_s = N_s\, h\nu_s\, d\nu_s$. Hence we have

$$\rho_\nu\, d\nu = \frac{8\pi\nu^2 d\nu}{c^3} \cdot \frac{h\nu}{e^{h\nu/kT}-1}. \quad . \quad . \quad . \qquad (49)$$

This represents the density of radiation between the frequencies ν and $\nu+d\nu$, which has already been deduced on p. 671 from different considerations by making use of hypothetical molecular resonators. Bose's treatment has the merit that nothing but photons or light-particles are used.

17·12. Thermodynamics of Particles with Spin—We have so long been working on the supposition that the atoms or molecules composing a gas are spherically symmetrical. But in nature, there are few atoms which can be said to conform to the ideal picture of structureless mass-points. As a matter of fact, it is well known that the atom is a highly complex system consisting of a central nucleus having a net positive charge ($+Ze$, Z=atomic number) surrounded by electrons arranged in definite groups according to a rule known as Pauli's Exclusion Principle. The reader should have a thorough knowledge of the principles of electron-structure of atoms in order that he may follow the arguments given below (see *Modern Physics* by Saha and Saha, p. 409).

The effect of this electronic structure is that very few atoms can be regarded as *spherically symmetrical.* The only exceptions are the inert gases He, Ne, A, Kr, Xe, Radon and the elements of the second group whose outer electrons form closed shells, which renders the atom magnetically neutral (diamagnetic). For example, He contains two electrons in the 1*s*-shell, which is denoted by the symbol $1s^2$ and the spins of the two electrons in the normal state are directed anti-parallel to each other, hence He-atoms are magnetically neutral. For the Ne-atom, the structure is $1s^2\ 2s^2\ 2p^6$; all layers form closed shells; and the atom is magnetically neutral. The lowest state is $^1S_0$. Atoms like He and Ne may be regarded as *spherically symmetrical*, i.e., conform to the picture of structureless mass-particles of our assumption. (*Vide* however p. 761.)

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[1] This can be written down directly from (15) if we remember that in case of photons $\alpha=0$, $f=1$, since the number of photons is not fixed and therefore the second of equations (13) does not exist.

But when we take the atom Na, it has the structure $1s^2 . 2s^2 . 2p^6 . 3s$, *i.e.*, it has one electron outside the closed shells. This electron endows the Na-atom with a definite magnetic moment; we say, in the language of atomic structure, that it is in the state $^2S_{1/2}$ and the atom behaves like a small magnet having the moment $eh/4\pi cm$ (Bohr-magneton). When it is placed in magnetic field, it sets itself with its axis parallel to the magnetic lines of force just as a small magnet does when suspended in the earth's field. But contrary to classical physics, it can also align itself, with equal probability and stability, anti-parallel to the field, *i.e.*, with its north pole pointing to the north pole of the field, as has been shown in Stern and Gerlach's experiments on *Directional Quantisation of Atoms.*

Generally speaking, an atom with a certain structure of its outer shell of electrons which is not complete, *e.g.*, fluorine with the structure $1s^2 . 2s^2 . 2p^5$. gives a number of states which can be easily written out with the aid of Pauli's principle. Thus F has the structure $2p^5$, and the normal states are $^2P_{3/2}$, $^2P_{1/2}$ with the energy difference $\Delta\nu = 410$ cm^{-1}. Normally fluorine gas consists of molecules, but if it were to occur in the form of atoms, they would be elementary magnets with the *inner quantum number* j, and the magnetic moment $\mu g j$ where μ=Bohr-magneton, g=Landé factor. Such an atom when placed in a magnetic field, is not only capable of setting itself parallel to the field, but may have its magnetic axis inclined at an angle θ to that of the external field, such that $\cos\theta = m/j$ where $m = j, j-1 \ldots, -j$; the number of m-values is $2j+1$, *i.e.*, $2\times\frac{3}{2}+1=4$. The energy of the atom for all these different orientations is the same; in the language of quantum mechanics, we say that the state is degenerate. If we apply an external magnetic field, the degeneracy is removed, *i.e.*, the atoms are divided into four groups with the small but finite energy difference $\Delta\epsilon = \mu g H j\,(1-\cos\theta)$. The number of positions which the atom can take up is $2j+1$, and this is known as the *Quantum-Weight g of the atom.* For Ne, we have $g=0+1=1$ *i.e.*, the atom is equivalent in all positions. For Na, it is $2.\frac{1}{2}+1=2$ and the free electron also has got the g value $= 2$, as it has a spin-axis. For F, $g=4$, for the normal state $^2P_{3/2}$, but 2 for the metastable state $^2P_{1/2}$.

It is now clear that the value of entropy of an assembly of particles like the fluorine atom will be rather different from that of an assembly of structureless particles. We can denote the different possible orientations by a, b . . and out of a totality of N particles, we can distribute

N_a to a, N_b to b, etc. . . . . When the magnetic field is not present we find that the disorder P is increased by

$$\frac{N\,!}{N_a\,!\;N_b\,!\ldots} \qquad \ldots \qquad (50)$$

The consequent increase in the value of entropy is

$$\Delta S = k \; ln \; \frac{N\,!}{N_a\,!\,N_b\,!\ldots} = -\mathrm{R} \sum \omega_r \; ln \; \omega_r ,$$

where $\omega_r = N_r/N$. For Na, we have $\omega_a = \omega_b = \frac{1}{2}$, hence $\Delta S = \mathrm{R}\; ln\; 2$. For Ne, $\Delta S = 0$. For a substance like F, $\Delta S = \mathrm{R}\; ln\; 4$; generally $\Delta S = \mathrm{R}\; ln\; g$, where $g =$ quantum weight.

We now take the consideration of Table 6, p. 478 where we left it. We find that for Zn, Cd, Hg, A, Ne the best agreement is obtained. These atoms are normally in the state $1s^2$, hence $g=1$, $\Delta S = \mathrm{R}\; ln\; g = 0$ and the chemical constant is given by formula (40), p. 477.

For Na, the results of previous workers were not at first very satisfactory. This was partly due to the fact that the Na-vapour was for long treated as entirely monatomic. Wood showed experimentally that Na-vapour gives an absorption band spectrum. Hence it must be partly diatomic. Ladenburg and Thiele investigated the vapour pressure between 496°C and 771°C with great care and calculated the fraction of molecules in the diatomic state. For full details the reader is referred to their original paper. For the Na-atom they found that $C_0 = \cdot 77 \pm \cdot 10$, From this we see (p. 478) that $C_0 - C_c = \cdot 32 \pm \cdot 10$, or if we put $\Delta C = \log g$, $\Delta S = \mathrm{R}\; ln g$, $g = 2$. This is in agreement with the fact that the statistical weight of the Na-atom is 2. For an atom whose normal state has statistical weight g, the expression for the chemical constant is

$$i = ln \left[\frac{(2\pi m)^{3/2}\; k^{5/2}}{h^3} \cdot g \right] ,$$

$$C = -1{\cdot}5885 + \tfrac{3}{2} \log M + \log g . \qquad \ldots \qquad (51)$$

Effect of Nuclear Spin.—Even the nucleus of the atom cannot be regarded as structureless. Modern researches have shown that it is a highly complex structure of protons and neutrons, and its structure is being slowly unravelled, but for our purpose a detailed knowledge of the structure is unnecessary. We are only concerned with the *Nuclear Spin* to which reference has already been made in §16·9. A nucleus with the spin moment zero, and surrounded by electrons forming close shells conforms to our picture of structureless mass points. But most atoms possess a definite spin moment i which endows its nucleus with a magnetic moment $i.g(i)\mu_p$, where $g(i)$ is the so-called *Landé factor* for the nucleus, and $\mu_p=\mu/1836$ the so-called protonic magnetic moment. The magnetic moment for the nucleus is therefore extremely small. In fact it is nearly 2000 times less than that of the electron. But its effect is to increase the disorder $(2i+1)$ times. Hence the expression for the entropy of a monatomic gas is further increased by the amount

$$\Delta S_n = R\, ln\, (2i+1) \quad . \quad . \quad . \quad . \quad . \quad (52)$$

But this term is without effect on the constant of the vapour pressure equation as the nuclei of atoms in the solid state also possess the same spin, and the entropy of the solid is to be increased by the same amount, *viz.*, by $\Delta S_n = R\, ln\, (2i+1)$. So the value of the chemical constant as deduced from the vapour pressure equation remains unchanged. But it should be taken into account while calculating the dissociation of a molecule, because the latter may have a different spin from the atom; also the entropy near the absolute zero of a solid may not be zero for solids composed of such atoms.

17·13. Thermodynamics of Di- and Poly-atomic Gases.—Following the methods given in this Chapter we can obtain all the thermodynamic properties of di- and poly-atomic gases.

For this, we have to consider the internal motion of molecules which, as we have seen in Chap XVI, are capable of rotation and vibration. Further the outer electrons of the molecule are capable of excitation, but this is a subject for which treatises on molecular spectra have to be consulted (*Vide* Herzberg, *Molecular Spectra*). The normal unexcited molecules can have spins resulting from electron configuration, just like atoms. The nuclei of their component atoms can have spins, which may combine in different ways forming resultant spins as in the case of Ortho- and Para-hydrogen. Let us consider first those molecules whose electronic spin is zero i.e., those known as ${}^1\Sigma_0$-molecules in spectroscopy, e.g. H_2 or N_2.

The value of probability of the whole state P is now

$$P = P_t .\ P_r .\ P_v .\ P_e \quad . \quad . \quad . \quad . \quad . \quad (53)$$

where P_t = probability for translational motion, already referred to. We take the classical probability given by (10); P_r, P_v, are respectively the probabilities for rotational and vibrational motion. We calculate these in the same way as in §17·2. But since the energies of rotational and vibrational motion are discrete, we have to calculate the number of cells a_r, a_v for any particular type of rotational and vibrational motion in a different way.

According to eqn. (4), p. 705 we have

$$p_\theta{}^2+p_\phi{}^2/\sin^2\theta = 2I\epsilon_s\,, \quad . \quad . \quad . \quad . \quad . \quad (54)$$

where $p_\theta = I\dot{\theta}$, $p_\phi = I\sin^2\theta.\ \dot{\phi}$. Now the volume of phase space enclosed by the surface of constant energy ϵ_s is

$$G=\int_0^\pi d\theta\int_0^{2\pi} d\phi\iint dp_\theta\, dp_\phi\;, \quad . \quad . \quad . \quad . \quad (55)$$

subject to the condition (54). The integral $\iint dp_\theta\, dp_\phi$ is the area of the ellipse represented by (54) and is therefore equal to $2\pi I\epsilon_s \sin\theta$. Hence (55) becomes

$$G= 2\pi I\epsilon_s\int_0^\pi \sin\theta\, d\theta\int_0^{2\pi} d\phi = 8\pi^2 I\epsilon_s = h^2 s(s+1), \quad . \quad (56)$$

since, as proved on p. 708, $\epsilon_s = s(s+1)h^2/8\pi^2 I$. The volume G_s of phase space described by the molecule, whose rotational motion is characterised by the quantum number s, is naturally the region of phase space contained between $s-\frac{1}{2}$ and $s+\frac{1}{2}$. Hence

$$G_s = h^2\left[(s+\tfrac{1}{2})(s+\tfrac{3}{2})-(s-\tfrac{1}{2})(s+\tfrac{1}{2})\right] = h^2(2s+1), \quad . \quad . \quad (57)$$

and

$$a_s = G_s/h^2 = 2s+1.$$

We can prove in a similar way that the value of $a_v=1$ and the value of $a_e=2j+1$, (see §17·12), where j is the inner quantum number of the electronic state of the atom or the molecule.

It can now be easily shown that in all these cases

$$P = N!\prod a^n/n!. \quad . \quad . \quad . \quad . \quad . \quad (58)$$

The particular subscript r, v, or e has to be affixed to the symbols P, a and n, when we are considering particular cases.

The argument is as follows: Let us take the rotational states. We have a_s positions for the s^{th} quantum state, and we have to put n_s particles in them. This can be done in $a_s{}^{n_s}$ ways The n_s particles can be chosen out of N in $N!/\Pi\, n_s!$ ways.

Multiplying we get (58). We do not divide[1] here by $N!$ as in the case of translational motion (Footnote p. 747). We have now[2]

$$\begin{aligned} S/k &= \sum_t n_t \, ln\,(a_t/n_t) + N + \sum_s \{N \, ln\, N + n_s \, ln\,(a_s/n_s)\} \\ &\quad + \text{two similar expressions for vibrational and electronic excitation} \\ &= (S_t + S_r + S_v + S_e)/k. \qquad (59) \end{aligned}$$

where S_t, S_r, S_v, S_e are the contributions to entropy by translational, rotational, vibrational and electronic motions respectively. Let us now find out the equilibrium values of n's. These are obtained from the conditions :

$$\delta S = 0, \qquad \delta N = 0, \qquad \delta U = 0, \qquad (60)$$

where S is given by (59), and N and U are given by

$$\left.\begin{aligned} N &= \sum n_t = \sum n_s = \sum n_v = \sum n_e = \text{constant.} \\ U &= U_t + U_r + U_v + U_e \\ &= \sum n_t \, \epsilon_t + \sum n_s \, \epsilon_s + \sum n_v \, \epsilon_v + \sum n_e \, \epsilon_e = \text{const.} \end{aligned}\right\} \qquad (61)$$

These give us the equations

$$\left.\begin{aligned} \delta S/k &= \sum \delta n_t . \, ln\,(a_t/n_t) + \sum \delta n_s . \, ln\,(a_s/n_s) + \sum \delta n_v \, ln\,(a_v/n_v) \\ &\qquad + \sum \delta n_e \, ln\,(a_e/n_e) = 0, \\ \delta U &= \sum \delta n_t . \, \epsilon_t + \sum \delta n . \, \epsilon_s + \sum \delta n_v . \, \epsilon_v + \sum \delta n_e . \, \epsilon_e = 0, \\ \delta N &= \sum \delta n_t = \sum \delta n_s = \sum \delta n_v = \sum \delta n_e = 0. \end{aligned}\right\} \qquad (62)$$

Now by the method of undetermined multipliers we have

$$\left.\begin{aligned} ln\,(a_t/n_t) - \alpha_t - \beta\epsilon_t &= 0, \\ ln\,(a_s/n_s) - \alpha_r - \beta\epsilon_s &= 0, \\ ln\,(a_v/n_v) - \alpha_v - \beta\epsilon_v &= 0. \end{aligned}\right\} \qquad (63)$$

Note that β is the same for all, as it comes in the energy-terms, but α_t, α_v, α_r are all different, as $\delta N = 0$ gives three different equations.

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[1] This is evident since the identity or interchange of molecules has to be considered only once, and this was done with translational motion.

[2] Note the difference in the expression for S/k between translational and other terms.

We have therefore

$$\left.\begin{aligned} n_t &= \frac{1}{f_t} a_t e^{-\beta\epsilon_t}, & n_s &= \frac{1}{f_r} a_s e^{-\beta\epsilon_s} \\ n_v &= \frac{1}{f_v} a_v . e^{-\beta\epsilon_v}, & n_e &= \frac{1}{f_e} a_e e^{-\beta\epsilon_e} \end{aligned}\right\} \quad . \quad . \quad (64)$$

where $$f_t = e^{\alpha_t},\ f_r = e^{\alpha_r},\ f_v = e^{\alpha_v},\ f_e = e^{\alpha_e}. \quad . \quad . \quad (65)$$

It can be easily proved as in §17·4 that $\beta = 1/kT$.

We can now find out the values of f_r, f_v, f_e. These are obtained from the conditions : $N = \Sigma n_s = \Sigma n_v$ etc. We have therefore[1] from (64), (65) and (61)

$$\left.\begin{aligned} N f_r &= \Sigma (2s+1)\ e^{-Bhs(s+1)/kT} &&= F_r \\ N f_v &= \Sigma\ e^{-vh\nu/kT} &&= F_v \\ N f_e &= \sum_j g_j\, e^{-(\epsilon_j - \epsilon_0)/kT} &&= F_e . \end{aligned}\right\} \quad . \quad (66)$$

The quantities F_r, F_v, F_e are known as Partition Functions (cf. p. 390).

We can now easily find out the values of S_r, S_v and S_e. From (59)

$$\begin{aligned} S_r/k &= \Sigma n_s\ ln\ (a_s/n_s) + N\ ln\ N \\ &= \Sigma\ n_s\,(ln\ f_r + \beta\epsilon_s) + N\ ln\ N \end{aligned}$$

from (64). Now we put $f = f_r/N$ etc. Then we see that

$$\frac{S_r}{k} = \frac{U_r}{kT} + \Sigma n_s\ ln\ F_r,$$

or $$S_r = \frac{U_r}{T} + \mathrm{R}\ ln\ F_r \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

We can obtain similar expressions for S_v and S_e. In the next sections, we give calculations of F_r, F_v, F_e.

We have now from (59) and (24)

$$S = \frac{\frac{5}{3} U_t + U_r + U_v + U_e}{T} + \mathrm{R}\ ln\,(f_t\, F_r\, F_v\, F_e) \,. \quad . \quad . \quad (68)$$

---

[1] Energies are measured with respect to the lowest energy state, hence the vibrational energy is put as $vh\nu$ instead of $(v+\frac{1}{2})h\nu$ and electronic energy as $\epsilon_j - \epsilon_0$.

17·14. Calculation of the Partition-functions.—We shall now evaluate F_r, F_V and F_e.

(a) PARTITION-FUNCTION FOR ROTATION

No general expression can be given for the partition-function for rotation. We can distinguish between the following cases :—

I. *Molecules with* $^1\Sigma$ *-fundamental state, but consisting of different nuclei, e.g., HCl, NaCl, HI.* For these molecules, we have

$$F_r = \sum_0^\infty (2s+1)\, e^{-s(s+1)\sigma} \quad \text{where } \sigma = h^2/8\pi^2 IkT.$$

When σ is a small quantity, it can be shown that the above expression reduces to

$$F_r = \frac{1}{\sigma} = \frac{8\pi^2 IkT}{h^2} \quad . \quad . \quad . \quad . \quad . \quad (69)$$

[Put $s(s+1)=x$. Then $F_r = \sum e^{-\sigma x}\frac{dx}{ds}\,ds$. Now F_r can be put equal to the integral $\int_0^\infty e^{-\sigma x}\,dx = \frac{1}{\sigma}$. The interval $ds=1$. The proof, however, is not rigorous].[1]

II. *Molecules in the* $^1\Sigma$ *-state with no nuclear spin, but with identical nuclei.* In such cases, only half the rotational terms are present. We have therefore

$$F_{rs} = \sum_{s=0,\,2,\,4..} (2s+1)\, e^{-s(s+1)\sigma}$$

$$F_{ra} = \sum_{s=1,\,3,\,5..} (2s+1)\, e^{-s(s+1)\sigma}$$

according as the para or the orthoform is present. It can be shown that for small values of σ, each of them reduces to $1/2\sigma$. We have then

$$F_r = 4\pi^2 IkT/h^2. \quad . \quad . \quad . \quad . \quad . \quad (70)$$

III. *Molecules in the* $^1\Sigma$ *-state, with identical nuclei, but the nuclei possess finite spin.* Examples : H_2, N_2, O_2.

For such cases, we have generally

$$F_{rs} \cdot F_{ra} = g_s \sum_{s=0,2,4..} (2s+1)\, e^{-s(s+1)\sigma} + g_a \sum_{s=1,3,5..} (2s+1)\, e^{-s(s+1)\sigma}$$

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[1] See further Mulholland, *Proc. Camb. Phil. Soc.*, **24**, 280, 1930.

because the gas is made up of molecules of two types, *para molecules* and *ortho molecules*, with even and odd values of s respectively. g_s and g_a are the weight factors due to nuclear spin. We have

$$g_a = i\ (2i+1),\quad g_s = (i+1)(2i+1),$$

if the nuclei obey Fermi-statistics, and

$$g_a = (i+1)(2i+1),\quad g_s = i(2i+1),$$

if the nuclei obey BE-statistics.[1] For proof see Note 11.

When σ is very small, each summation of odd or even terms reduces to $1/2\sigma$, and we obtain

$$F_r = (2i+1)^2/2\sigma. \quad . \quad . \quad . \quad . \quad (71)$$

As we have seen, σ is generally very small for all gases excepting H_2 and such others which have the H-atom as one constituent. These cases require special treatment.

IV. *Molecules in other than* $^1\Sigma$*-state.*—For such cases, special papers should be consulted. The treatments are far too complex to be given in a text-book.

(*b*) PARTITION-FUNCTIONS FOR VIBRATION

In the case of heavy molecules, the vibrational modes of freedom may also be excited. We have from (66)

$$F_v = \Sigma e^{-vh\nu} = \left(1-e^{-h\nu}\right)^{-1} \quad . \quad . \quad . \quad (72)$$

(*c*) PARTITION-FUNCTIONS FOR ELECTRON-EXCITATION

The value of F_e is given by

$$F_e = g_0 + \sum g_j\ e^{-(\epsilon_j-\epsilon_0)/kT}, \quad . \quad . \quad . \quad . \quad (73)$$

where g_0=weight of the fundamental electronic state, g_j=weight of any excited state, $\epsilon_j-\epsilon_0$ is the energy of excitation.

For most molecules and atoms the energy of excitation of higher states is so great that none but the first term need be taken into account. But there are exceptions too.

17·15. The Thermodynamical Functions for di- and polyatomic substances and for electron excitation.—With the aid of (68), we can find out the values of entropy and other thermodynamical functions of di- and polyatomic substances and also for electron excitation of atoms and molecules.

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[1] Nuclei with odd mass numbers obey F. D-statistics; those with even mass number obey B.E-statistics (see Note 11.)

Let us first take a diatomic molecule for which only the rotational degrees of freedom are fully excited, but neither the vibrational nor electronic motion is excited. We have now

$$U_r = RT, \qquad F_r = 8\pi^2 IkT/h^2.$$

We have therefore from (68)

$$\left.\begin{aligned} \frac{S}{R} &= \frac{7}{2}\, ln\, T - ln\, p + ln \left[\frac{(2\pi m)^{3/2}\, k^{5/2}\, e^{5/2}}{h^3} \cdot \frac{8\pi^2 Ike}{h^2}\right]. \\ \frac{\Psi}{R} &= \frac{7}{2}\, ln\, T - ln\, p + ln \left[\frac{(2\pi m)^{3/2}\, k^{5/2}}{h^3} \cdot \frac{8\pi^2 Ik}{h^2}\right] - \frac{U_0}{RT} \end{aligned}\right\} \quad (74)$$

An application of these formulae is given in §17·16.

Partition function for nuclear spin.—Fowler and Sterne have given the following useful table for F_n for different types of molecules when they obey the Fermi-statistics.

Table 1.—*Partition function for nuclear spin for different molecules.*

Type	Para X_2	Ortho X_2	Heteronuclear X_2	XY
$^1\Sigma$	$\frac{1}{2}i\,(2i+1)$	$\frac{1}{2}(i+1)(2i+1)$	$2(2i_1+1)(2i_2+1)$	$(2i_1+1)(2i_2+1)$
$^3\Sigma\,(O_2)$	$\frac{3}{2}i(2i+1)$	$\frac{3}{2}(i+1)(2i+1)$	$3(i_1+1)(2i_2+1)$	$3(2i_1+1)(2i_2+2)$

The discussion shows that it is impossible to give a general formula for the calculation of the entropy of a diatomic gas. Every case must be treated on its own merits. We shall illustrate this by taking a few typical cases.

17·16. Vapour Pressure of Diatomic Substances.—With the aid of the expressions for entropy and the ψ-function of diatomic substances given in the previous sections, it is possible to obtain a theoretical expression for the vapour pressure of these substances within limited ranges. We suppose that the temperature is high enough for the excitation of the rotational degrees of freedom, but the vibrational or electronic motion is not excited. The procedure is exactly as in §11·21. We start with the equation $\psi_{cond} = \psi_{gas}$.

The expression for Ψ_{cond} is exactly the same as (33) of §11·21. For the value of Ψ_{gas} we have to utilise an expression, suitable to the case out of those given in §17·15. We thus obtain for a molecule of type I, p. 766,

$$ln\, p = -\frac{\lambda_0}{RT} + \frac{7}{2}\, ln\, T - \frac{1}{R}\int_0^T \frac{dT}{T^2}\int_0^T C_p\, dT$$

$$+ \, ln\left[\frac{(2\pi m)^{3/2}\, k^{5/2}}{h^3} \cdot \frac{8\pi^2 Ik}{h^2}\right] - \frac{S_0}{R},$$

where S_0 = null-point entropy of the solid. For convenience of practical work, it can be put in the form

$$\log p = -\frac{\lambda_0}{2{\cdot}3RT} + \frac{7}{2}\log T - \frac{1}{2{\cdot}3R}\int_0^T \frac{dT}{T^2}\int_0^T (C_{p,s})\, dT$$

$$+ 36{\cdot}815 + \frac{3}{2}\log M + \log I - \frac{S_0}{2{\cdot}3R}, \quad . \quad . \quad . \quad (75)$$

where M is the molecular weight of the gas.

Experimental Verification of the Vapour-pressure Formula—The chemical constant C now has the value

$$C = 36{\cdot}815 + \frac{3}{2}\log M + \log I - \frac{S_0}{2{\cdot}3R}, \quad . \quad . \quad . \quad (76)$$

and it can be subjected to test provided the vapour-pressure is known over a sufficiently wide range. The test has been carried out by Eucken and his pupils; Clusius, Simon, Giauque in America and their results are shown in Table 2.

Table 2.—*Chemical constant of some diatomic gases.*

Substance	Ground State	$I \times 10^{40}$ gm. cm^2	Observed Chemical Constant	Chemical Constant (Calc.)
H_2	$^1\Sigma$	·466	—3·68±0·03	—3·722
N_2	$^1\Sigma$	13·8	—0·16±0·03	—0·177
HCl	$^1\Sigma$	2·656	—0·40±0·03	—0·419
HBr	$^1\Sigma$	3·32	0·24±0·04	0·197
HI	$^1\Sigma$	4·31	0·65±0·05	0·608
Cl_2 ($Cl^{35}\,Cl^{35}$)	$^1\Sigma$	114	1·66±0·08	1·352
Br_2	$^1\Sigma$	445	2·59±0·10	2·467
I_2	$^1\Sigma$	820	3·08±0·05	3·031
O_2	$^3\Sigma$	19·15	0·55±0·02	0·530
NO	$^2\pi$	16·4	0·55±0·03	(110°K) 0·479 (2400°K) 0·681
CO	$^1\Sigma$	15·0	—0·07±0·05	0·160

17·17. Chemical Constant of Hydrogen.—It was found by Eucken that hydrogen and its compounds always show a tendency not to obey the Nernst Heat Theorem. For example, Eucken calculated that the value of the chemical constant of H_2 deduced from the vapour pressure data at a low temperature (upto 20°K) is $-1 \cdot 09$, while its value deduced from the vapour pressure data at 80°K is $-3 \cdot 68$. This discrepancy was explained by Fowler and Sterne from Dennison's theory of pH_2 and oH_2. A brief sketch of the theory in the notation of this book is given below.

Chemical Constant of Hydrogen at low temperature.—To explain the observed value of the chemical constant at very low temperature, we suppose that even the rotational degrees of freedom are not excited. We can therefore regard H_2 as a monatomic gas of atomic weight 2·015. Now provided that for the solid we can take $S_0=0$, we have

$$i_{H_2} = (2\pi m)^{3/2} k^{5/2}/h^3 \text{ where } m=2 \cdot 015/6 \cdot 06 \times 10^{23}.$$

It is easy to see that the value of the chemical constant is given by

$$C_{H_2} = -\ 1 \cdot 5885 + \frac{3}{2} \log 2 \cdot 015 = -1 \cdot 132. \quad . \quad . \quad (77)$$

This value is in very good agreement with Eucken's experimental value.

The assumption $S_0=0$ is, as we shall see presently, true only for pH_2; on the other hand oH_2, as it possesses a finite nuclear moment ($i=1$) and the rotational moment $h/2\pi$, would have a null-point entropy. The calculation has been given in Chap. XVI. But whatever may be the constitution of condensed H_2 (proportion of pH_2 and oH_2 composing it), it is obvious that equivalent proportions of pH_2 and oH_2 would evaporate from the solid. In the case of oH_2, the value of i_{H_2} would be larger but as the null-point entropy is larger by the same amount, the value of the chemical constant would remain unaffected.

Chemical Constant at higher temperatures.—At temperatures of the order 80°K the rotational degrees of freedom are fully excited but the vibrational motion can be neglected. The condensed phase may be regarded as consisting of x parts of pH_2 and $1-x$ parts of oH_2. We may suppose that in the evaporated gas also, the molecules are present in the same ratio. The calculation of the chemical constant becomes complex. The best way of approaching the problem is first to calculate the value of the chemical constant for each constituent separately, assuming that both the condensed phase and the gas consist of only one type.

(*a*) For pH_2, $F_r = 1/2\sigma$, $F_n=1$, and we obtain from (74)

$$\frac{\Psi_{pH_2}}{R} = \frac{7}{2}\, ln\, T - ln\, p + ln \left[\frac{(2\pi m)^{3/2}\ k^{5/2}}{h^3} \cdot \frac{8\pi^2 Ik}{h^2} \cdot \frac{1}{2} \right] = \Psi_0 - ln\, 2.$$

The value of the chemical constant is easily seen to be.

$$C_{pH_3} = 36\cdot815 + \frac{3}{2}\log M + \log I - \log 2 = C_0 - \log 2, \quad . \quad (78)$$

where C_0 is put for $36\cdot815 + (3/2)\log M + \log I$. The value of C_0 is easily seen to be $-3\cdot059$, since $M = 2\cdot015$, $I = \cdot467\times10^{-40}$ gm. cm².

(*b*) For oH_2, $F_r = 1/2\sigma$, $F_n = 3$, and we obtain from (74)

$$\Psi_{oH_2} = \Psi_0 + ln\,3 - ln\,2,$$

and
$$C_{oH_2} = C_0 + \log 3 - \log 2 = -2\cdot883. \quad . \quad . \quad (79)$$

Now the entropy of a mixture of x parts of pH_2 and $(1-x)$ parts of oH_2 is according to (27) of p. 317 given by

$$S = x\,[C_p\,ln\,T - R\,ln\,px + i_{pH_2}] + (1-x)\,[C_p\,ln\,T - R\,ln\,p(1-x) + i_{oH_2}]$$
$$= C_p\,ln\,T - R\,ln\,p - x\,ln\,x - (1-x)\,ln\,(1-x) + xi_{pH_2} + (1-x)\,i_{oH_2}.$$

Hence we find that the chemical constant of the mixture is given by

$$C_{H_2} = -x\log x - (1-x)\log(1-x) + x\{C_0 - \log 2\}$$
$$+ (1-x)\{C_0 + \log 3 - \log 2\}$$
$$= C_0 - [x\log x + (1-x)\log(1-x) + \log 2 - (1-x)\log 3].$$

If we put $x = 1/4$, it is easy to see that

$$C_{nH_2} = C_0 - \log 2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (80)$$

We have obtained this value on the assumption that the value of entropy of the condensed phase at the A.N. is zero. This would be the case if the whole mass consisted of pH_2, for in this case at the A.N., $F_r = 1$ as the molecules are all in the zeroth rotational state, and $F_n = 1$, since $i = 0$. We have $F_r.F_n = 1$, and $S_0 = 0$. But for oH_2 at the A.N., $F_r = 3$ as all the molecules have the rotational quantum number $s = 1$ and $F_n = 3$, as $i = 3$. We have $F_r.F_n = 9$ and $S_0/R = ln\,F_r.F_n = ln\,9$.

Let us now take a mixed crystal consisting of x parts of pH_2 and $(1-x)$ parts of oH_2. We have at the A.N.

$$S_0/R = x\,ln\,1 + (1-x)\,ln\,9 - [x\,ln\,x + (1-x)\,ln\,(1-x)]$$
$$= -[x\,ln\,x + (1-x)\,ln\,(1-x) - (1-x)\,ln\,9]. \quad . \quad . \quad (81)$$

The additional term within the braces [ ] arises from the fact mentioned above that out of a totality of N particles, Nx has the orientation of pH_2 and $N(1-x)$ of oH_2. The disorder P is increased by $\dfrac{N!}{Nx!\,N(1-x)!}$ and the corresponding increase in entropy is given by the relation

$$\Delta S/R = -x\,ln\,x - (1-x)\,ln\,(1-x)$$

as in §9·4.

If $x = 1/4$, we get from (81),

$$\frac{S_0}{R} = \frac{3}{4} \, ln \, 3 + ln \, 4 \quad \text{(null-point entropy of } nH_2\text{)}.$$

The value of the chemical constant, as obtained from vapour pressure measurements, should have the value

$$\begin{aligned} C_{nH_2} &= C_0 - [x \log x + (1-x) \log(1-x) + \log 2 - (1-x) \log 3] \\ &\quad + [x \log x + (1-x) \log (1-x) - (1-x) \log 9] \\ &= C_0 - \log 2 - (1-x) \log 3. \qquad (82) \end{aligned}$$

For $x=1/4$, we have

$$C_{nH_2} = C_0 - \log 2 - \tfrac{3}{4} \log 3 = -3{\cdot}059 - {\cdot}659 = -3{\cdot}718. \qquad (83)$$

This agrees well with Eucken's value $-3{\cdot}68 \pm {\cdot}03$.

The extraordinary complexity of the case of H_2 is thus traced to the fact that it exists in two forms pH_2 and oH_2, and the usual gas or solid is a mixture of the two.

17·18. Emission of Electricity from Incandescent Solids.—It was discovered early in the present century that all bodies when sufficiently heated emit "electrons," and thanks to the pioneering investigations of O. W. Richardson, followed by I. Langmuir, Dushman and others, the laws and other characteristics of electron emission are now pretty accurately known. For detailed study, many texts are at present available.[1]

In 1918, M. von Laue[2] showed that the problem can be treated as a case of evaporation of the electron gas from the state of condensed phase inside the metal to that of the gaseous phase. It can therefore be treated as a heterogeneous chemical reaction. All carbonates when sufficiently heated emit CO_2; similarly all matter, when heated, emit electrons, as these are common constituents of all matter. We can treat the problem from the thermodynamical point of view. For equilibrium, we have

$$\psi_{e,\,\text{gas}} = \psi_{e,\,\text{cond}}. \qquad (84)$$

According to equations (36) and (33) of Chap. XI we have

$$\psi_{e,\,\text{gas}} = C_{p,e} \, ln \, T - R \, ln \, p_e + R \, ln \left[\frac{(2\pi m)^{\frac{3}{2}} \, k^{\frac{5}{2}}}{h^3} \, g \right] - \frac{U_{e,0}}{T}$$

$$\psi_{e,\,\text{cond}} = - \frac{U_{e,\,\text{cond.}}}{T} + \int_0^T \frac{dT}{T^2} \int_0^T C_{p,\,e}' \, dT,$$

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[1] O. W. Richardson, *Emission of Electricity from Hot Bodies*; Dushman, *Reviews of Modern Physics*, **2**, p. 381; *Thermionic Emission* by Reimann.

[2] M. von Laue, *Ann. d. Physik*, **51**, 695, 1919.

where $C_{p,e}$ is the specific heat of electron gas at constant pressure and $C_{p,'e}$ is the specific heat at constant pressure of electrons inside the metal.

Hence from (84) we get

$$ln\, p_e = -\frac{\lambda_0}{RT} + \frac{C_{p,e}}{R}\, ln\, T + ln\left[\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}\, g\right]$$

$$-\frac{1}{R}\int_0^T \frac{dT}{T^2}\int_0^T C_{p',e}\, dT, \quad . \quad . \quad . \quad (85)$$

where λ_0 denotes the latent heat of evaporation of the electron at A.N.

If we put $C_{p,'e}=0$, (85) reduces to

$$ln\, p_e = -\frac{\lambda_0}{RT} + \frac{5}{2}\, ln\, T + ln\, 2I, \quad . \quad . \quad . \quad (86)$$

since $C_{p,e} = \frac{5}{2}R$, $g_e=2$. Now $I = \frac{(2\pi m)^{\frac{3}{2}}\ k^{\frac{5}{2}}}{h^3}$, therefore

$$n_e = 2.\frac{(2\pi mk)^{\frac{3}{2}}}{h^3}.\, T^{\frac{3}{2}}\, e^{-\lambda_0/RT} \quad . \quad . \quad . \quad (87)$$

In actual practice we measure the saturation current. We may suppose that the surface of the wire is covered with free electrons exerting a pressure p_e, which are then effusing into vacuum. The velocity of efflux v_0 is given by (see p. 193)

$$v_0 = \frac{1}{4}\bar{c} = \sqrt{\frac{kT}{2\pi m}}.$$

The saturation current

$$i = nev_0 = \frac{4\pi mk^2e}{h^3}T^2\, e^{-\lambda_0/RT} = A_0T^2\, e^{-\lambda_0/RT} \quad . \quad (88)$$

where putting proper values for m, k and h we obtain

$$A_0 = \frac{4\pi emk^2}{h} = 120{\cdot}4 \text{ amp./cm.}^2\text{deg.}^2$$

For experimental verification of (88) and critical discussion see Dushman or Reimann, *loc. cit.*

Comments.—The assumption that $C_{p,'e}$ the specific heat at constant pressure of electrons inside the metal is zero at high temperatures, which is implicitly involved in the above deduction, is however open to doubt and is certainly opposed to facts.

17·19. The Nernst Heat Theorem: A Historical Account.—This theorem arose out of the quest to find out the conditions which lead a chemical reaction to completion. We saw in §8·5 how for an isothermal-isochoric reaction Gibbs and Helmholtz obtained the relation

$$F^* - T\frac{dF^*}{dT} = U,^* \quad . \quad . \quad . \quad . \quad . \quad (89)$$

where F^* denotes the decrease in the free energy during the molecular reaction and U^* is the decrease in internal energy i.e. the heat of reaction. As described on p. 345 for reactions taking place in a galvanic cell, F^* is measured by the E.M.F. of the cell. We shall illustrate the Nernst Heat Theorem (N.H.T.) by considering the processes in a galvanic cell.

Suppose now we set to ourselves the task of finding out theoretically how E or F^* varies with temperature, particularly at low temperatures. It is clear from (89), that we must find out how U^* and dF^*/dT vary with temperature. We have $dU^*/dT = \Sigma nC$ where C is the molar specific heat of the components taking part in the reaction, taken with the proper sign for the summation and n is the number of mols. For a concrete example, vide supra. We have therefore

$$U^* = U^*_0 + \int_0^T \Sigma nC\, dT. \quad . \quad . \quad . \quad . \quad . \quad (90)$$

U^* can be calculated as a function of T provided we know, either empirically or from theoretical considerations, how C varies with T. In the earlier days, empirical formulæ were much used. Now-a-days, it is more convenient to use the Debye formula.

Calculation of F^* :—Looking back on equation (89) we find that our next task is to find out dF^*/dT. We have, on differentiating (89),

$$-T\frac{d^2F^*}{dT^2} = \frac{dU^*}{dT} = \Sigma nC.$$

Hence by integration, we have

$$\frac{dF^*}{dT} = -\int_0^T \frac{\Sigma nC}{T}\, dT + \left(\frac{dF^*}{dT}\right)_0 \quad . \quad . \quad . \quad . \quad (91)$$

The first term can be easily calculated since the variation of C with T is known. But the integration constant presents difficulties. An exact knowledge of its value is essential for the calculation of dF^*/dT as well as of F^* but no clue, theoretical or experimental, was available as to how it could be determined. At this point, Nernst enunciated his Heat Theorem (1906). Now $\left(\frac{dF^*}{dT}\right)_0 = \triangle S_0$, the change in the entropy value of the system at the A. N. when a unit reaction is allowed to take place. Nernst proposed that this should be put equal to zero, *i.e.*,

"*At the absolute null-point, all reactions in condensed systems proceed without change in the value of the total entropy of the system.*"

If this relation be correct, we have from (89), (90) and (91)

$$F^* = U^*_0 + \int_0^T \Sigma nC\, dT - T\int_0^T \frac{\Sigma nC}{T} dT$$

$$= U^*_0 - T\int_0^T \frac{dT}{T^2}\int_0^T \Sigma nC\, dT. \quad . \quad . \quad . \quad . \quad (92)$$

This relation enables us to determine F^* at any temperature.

According to the Heat-Theorem, we have thus

$$F^*_0 = U^*_0,\ \left(\frac{dF^*}{dT}\right)_0 = 0, \text{ and } \left(\frac{dU^*}{dT}\right)_0 = 0\ . \quad . \quad . \quad (93)$$

We can thus summarize the advance in knowledge regarding the energy-relations in these reactions.

According to Berthelot, F^* was equal to U^* at all temperatures, but Gibbs and Helmholtz found this to be erroneous, and showed that $F^* = U^*$ only at the A.N. Nernst goes still further. He shows that not only is $F^* = U^*$ at the A.N., but both dF^*/dT and dU^*/dT vanish at the A.N. Thus the F^* and U^* curves become horizontal and touch each other at the A.N. This is shown in the accompanying diagram (Fig. 1).

It may be noted that while the condition $(\partial F^*/\partial T)_0 = 0$ is necessary and sufficient for the deduction of the integral form of the Gibbs-Helmholtz equation, the condition $(\partial U^*/\partial T)_0 = 0$ is only necessary, but not sufficient. For, from the condition $(\partial F^*/\partial T)_0 = 0$ we can deduce that $(\partial U^*/\partial T)_S = 0$ as shown above but not *vice versa*; *i.e.*, if we assume $(\partial U^*/\partial T)_0 = 0$, it does not follow that $(\partial F^*/\partial T)_0 = 0$.

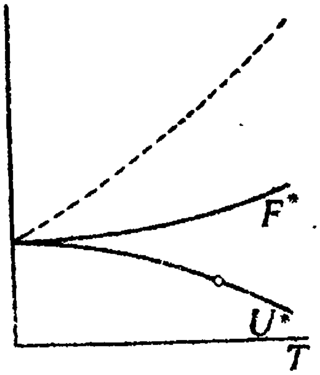

Fig. 1.—Variation of F^* and U^* with temperature.

The dotted curve illustrates a hypothetical case where $(\partial F/{}^*\partial T)_0 \neq 0$. This differentiation is necessary because we now know from Debye's and other theories of specific heat that $(\partial U^*/\partial T)_0 = \Sigma nC$ tends to vanish at the A.N. for all condensed phases, and from this we may be tempted to infer that no further condition is needed to integrate the Gibbs-Helmholtz equation. The condition $(\partial F^*/\partial T)_0 = 0$ *goes further and is essential.*

Illustration:—Let us take for the sake of illustration the element

$$\text{Pb} \mid \text{Pb Cl}_2 \mid \text{Ag Cl} \mid \text{Ag}$$

The reaction is

$$\mid \text{Pb} \mid + 2\,(\text{AgCl}) = (\text{PbCl}_2) + 2 \mid \text{Ag} \mid$$

The energy evolved can be calculated from the two following well-determined heats of solution at 17°C or 290°K.

$$\mid \text{Pb} \mid + 2(\text{HCl}) = (\text{PbCl}_2) + \text{H}_2 + 85700 \text{ cal.}$$

$$\mid \text{Ag} \mid + (\text{HCl}) = (\text{AgCl}) + \tfrac{1}{2}\text{H}_2 + 30410 \text{ cal.}$$

Combining the two we get

$$\mid \text{Pb} \mid + 2(\text{AgCl}) = 2 \mid \text{Ag} \mid + (\text{PbCl}_2) + 24880 \text{ cal.}$$

Thus $U^*_{290} = 24 \cdot 88$ k. cal., and it can be shown that this value is in agreement with the Gibbs-Helmholtz law connecting the e.m.f. (E) of the cell, and U^*. For according to the careful measurements of Brönsted, the variation of e.m.f. with temperature is given by the empirical formula

$$E = \cdot 4917 - \cdot 000165t \ (t = \text{degrees centigrade}).$$

Hence
$$\frac{U^*}{23060 \times 2} = E - T\frac{dE}{dT} = \cdot 5367,$$

$$\text{or} \quad U^* = 24 \cdot 73 \text{ k. cal.}$$

Thus the Gibbs-Helmholtz law is satisfied.

The variation of U^* with T in this particular case is given according to (90) by

$$\frac{dU^*}{dT} = \Sigma nC = C_{Pb} + 2C_{AgCl} - 2C_{Ag} - C_{PbCl_2}$$

and now we can find out U^*_0, with the help of equation (90). We have

$$U^*_0 = U^*_{290} - \int_0^T C_{Pb}\,dT - 2\int_0^T C_{AgCl}\,dT + \int_0^T C_{PbCl_2}\,dT + 2\int_0^T C_{Ag}\,dT.$$

Now the values of C have been determined almost up to the A.N. We can represent C by Debye functions and then evaluate the integrals mathematically or we can carry out the integration by the graphical method. The use of Debye functions gives us

$$U^*_0 = U^*_{290} - 1596 - 5448 + 1545 + 4966 + \text{some minor terms}$$
$$= 24\cdot88 - \cdot60 \text{ k. cal.} = 24\cdot28 \text{ k. cal.}$$

The value of U^*_0, calculated by Miething according to the graphical method is 24·33 k. cal.

Let us now calculate F^*_0. We have from (93)

$$F^*_0 = F^* + T\sum\int_0^T \frac{dT}{T^2}\int_0^T nC\,dT \; . \quad . \quad . \quad (94)$$

the summation being taken for $-$ Pb, $-$ 2AgCl, $PbCl_2$, 2Ag.

We can evaluate the integrals by Debye functions or graphically. From the first method we get

$$\sum\int_0^T \frac{dT}{T^2}\int_0^T C\,dT = 9\cdot75 + 26\cdot6 - 9\cdot92 - 19\cdot1 + \text{minor terms} = 7\cdot60 \text{ cal.}$$

Hence $F^*_0 = 22\cdot54 + 290 \times \cdot0076 = 24\cdot74$ and $U^*_0 - F^*_0 = \cdot52$.

On the other hand, using the graphical method we get

$$F^*_0 = 24\cdot40 \text{ and } U^*_0 - F^*_0 = -\cdot20.$$

The graphical method is more satisfactory as the correcting factors are automatically taken care of.

Thus we verify that within experimental errors, $F^*_0 = U^*_0$. The assumption $(\partial F^*/\partial T)_0 = 0$ is already contained in the formula (94) for F^*_0.

For further verification of the N. H. T. in the thermodynamics of cell-reactions, the following books may be consulted:—Jellinek, *Lehrbuch der physikalischen Chemie*, Vol. 3, pp. 750—760; Lewis and Randall, *Thermodynamics*, Chap. XXXI.

Planck's Formulation of the Nernst Heat Theorem.—In 1910, Planck went a step further, and formulated that not only is the aggregate change in entropy

$$\Delta S = \sum nS_0 = 0$$

for the whole reaction, but the value of entropy for each condensed phase vanishes individually at the absolute zero. Applying to the reaction just treated we have, according to Planck,

$$(S_{Pb})_0 = 0. \quad (S_{PbCl_2})_0 = 0, \quad (S_{Ag})_0 = 0, \quad (S_{AgCl})_0 = 0,$$

and similarly for every condensed phase at 0°K,

$$S_0 = 0. \; . \quad . \quad . \quad . \quad . \quad . \quad (95)$$

In the foregoing we have given the historical development of N.H.T., its formulation by Planck and its experimental verification for condensed systems by calculating the free energies. The N. H. T. has been verified for various other reactions in condensed systems, and also for condensed systems in equilibrium with the gaseous phase by calculating the entropies. To the latter class belong the verification given in §11·22 which is based on the assumption of N. H. T. and provides a simultaneous check on statistical theory and the heat theorem. For equilibria involving polyatomic gases the method usually adopted is to calculate the equilibrium constant of the reaction in terms of the vapour pressure constants or chemical constants. For details of this verification see *Introduction to Modern Thermodynamical Principles* by Ubbelohde (Clarendon Press, Oxford, 1937), pp. 26—47. It has been found that for such solids which can be shown to be composed of spherically symmetrical particles, the theorem agrees with experimental results. Departures have been found only in such cases where the entropy, even at the lowest temperature, is positive due to nuclear spin and isotopic rearrangement. This has led Fowler to examine critically the basis of N. H. T. from statistical mechanics and state the theorem in the form:

"For any isothermal process involving only phases in internal equilibrium, or alternatively, if any phase is in metastable equilibrium, provided the process does not disturb this frozen equilibrium $\underset{T\to 0}{Lt} \triangle S=0$."

Fowler considers the principle of the *unattainability of the absolute zero*, first given by Nernst in 1912, as more fundamental and elevates it to the position of a fundamental law—the *Third Law of Thermodynamics* stating it in the form:

"It is impossible by any procedure, no matter how idealized, to reduce any assembly to the absolute zero in a finite number of operations." For details of discussion see Fowler and Guggenheim, *Statistical Thermodynamics*, (C. U. P. 1939) pp 218—229. It is easy to deduce the Third Law from Nernst Heat Theorem or vice versa.

Recently the concept of negative absolute temperatures has been given by an application of thermodynamics to nuclear processes. For details see Ramsay, *Phys. Rev.*, **103**, 20, 1956.

Books Recommended

Same as in Chap. IX.

CHAPTER XVIII

THERMODYNAMICS OF CHEMICAL EQUILIBRIA

18·1. Thermodynamical Treatment of Chemical Reactions.—Chemical Reactions form a very large class of phenomena which can be treated by thermodynamical methods, evolved in §8·9, where they have been applied to simple physical processes like evaporation or sublimation. Let us briefly describe the general features of such reactions.

Let us bring together two chemical substances which can react with each other, say H_2 and S. They will proceed to combine with each other forming H_2S, but experience tells us that the reaction is never complete. There always remains some amount of uncombined H_2 and S-vapour. This can be readily seen by heating H_2S to about 400°C, when sulphur is deposited and a proportionate amount of H_2 is set free. It is found that the proportions of H_2S and uncombined H_2 and S-vapour depend upon temperature and pressure of the system. We further picture that when molecules of H_2 and S come together, some of them combine to form H_2S and similarly an equal number of H_2S-molecules break up into H_2 and S molecules. The state of affairs is expressed by the symbolical equation introduced by Van't Hoff, viz.

$$H_2+S \rightleftarrows H_2.$$

Even in cases like the formation of H_2O-vapour out of H_2 and O_2, where the chemical reaction seems to be complete, careful investigation shows that there is always some free H_2 and O_2; the proportion of which increases with temperature.

Reaction Stage and Equilibrium Stage of Homogeneous Reactions.—Chemical reactions can take place between two substances when either or both of them are gaseous, liquid or solid or in solution. The reaction is said to be homogeneous when all the reacting species are in the gaseous state, or in solution. When one or both are in other states, it is said to be heterogeneous. In this chapter we shall deal chiefly with ***homogeneous*** *reactions.* There are two stages to deal with : (1) a reaction stage, (2) an equilibrium stage.

Chemical reaction does not immediately set in directly two reacting substances are brought together. For example H_2 and O_2 gas may be kept together for hours, days, nay even for months, and even then may not appreciably combine with each other. If however a spark is passed, they will combine with great rapidity forming H_2O; but after the equilibrium condition has once been attained, further sparking will not alter the relative proportions of H_2, O_2 and H_2O. The spark thus stimulates the reaction. In fact the majority of chemical reactions proceed very slowly under ordinary conditions. But in the presence of certain foreign substances, called *catalysts*, the reaction takes place quickly though the catalyst apparently takes no part in the reaction. Examples of these will be found in any book on chemistry. It may be however mentioned that though the velocity of both the direct and the reverse reaction [i.e. values of k_1 and k_2 in equation (7)] may be increased by the presence of *catalysts*, the final equilibrium concentrations remain unaltered. This is particularly so when the catalyst is present only in small quantities and is unable to affect the activity of the reacting substances.

The treatment of the equilibrium stage follows that given in §8·9. The temperature is taken to have the same value throughout the whole reaction space, and the state of equilibrium is given by the condition : $\delta F=0$, $\delta G=0$ depending upon whether the permitted reaction is isothermal-isochoric, or isothermal-isobaric, δ denoting a virtual infinitesimal change of the system consistent with the external constraints. It should however be pointed out that there are many cases where these conditions do not hold. Reactions may be taking place in a space where temperature varies from point to point, or the constituents may not be at the same temperature. These cases of deviation from thermodynamical equilibrium are difficult to treat and no account of these will be given here.

18·2. Symbolism used in Chemical Equilibria.—The symbols used to describe chemical equilibria are numerous, and sometimes perplexing. Let us explain them at the outset.

The general reaction[1] is represented by the symbol

$$a_1 A_1 + a_2 A_2 + \ldots a_r A_r + \ldots \rightleftarrows b_1 B_1 + b_2 B_2 + \ldots b_s B_s + \ldots \quad (1)$$

This implies that a_1 mols of A_1, a_2 mols of A_2 etc. react with each other, and yield b_1 mols of B_1, b_2 mols of B_2 etc. The symbol $\rightleftarrows$ denotes that the reaction proceeds both ways.

We further represent by

N......the total number of molecules in the vessel.
λ............................mols................
N_{Ar}, N_{Bs} ....molecules of types A_r, B_s
λ_{Ar}, λ_{Bs} ....mols of ....
n_{Ar}, n_{Bs} ....particles per unit vol. of A_r, B_s
ν..........................mols per unit vol.
ν_{Ar}, ν_{Bs}.....................mols per unit vol. of A_r, B_s
p...........the total pressure in the reaction-vessel
p_{Ar}, p_{Bs} ......the partial pressures of A_r, B_s, etc....
x_{Ar}, x_{Bs} ......the partial concentrations or mol-fractions of A_r, B_s etc.
U_{Ar}, U_{Bs} the internal energies of unit mol of A_r, B_s.

We have then

$$\left.\begin{aligned} x_{Ar} &= \frac{N_{Ar}}{N} = \frac{n_{Ar}}{n} = \frac{\lambda_{Ar}}{\lambda} = \frac{\nu_{Ar}}{\nu}, \quad \nu_{Ar} = \frac{\lambda_{Ar}}{V} \\ \text{and} \quad p_{Ar} &= \nu_{Ar}.RT = n_{Ar}.kT = x_{Ar}.p, \; p = \Sigma(p_{Ar} + p_{Bs}) \end{aligned}\right\} \quad (2)$$

18·3. Application of the First Law of Thermodynamics. Heats of Reaction and their variation with temperature.—The total internal energy of the system is given by

$$\mathrm{U} = \Sigma \lambda_{Ar}.U_{Ar} + \Sigma \lambda_{Bs}.U_{Bs}. \quad (3)$$

Hence the change in the total internal energy due to the reaction (1) taking place is given by

$$\Delta\mathrm{U} = \Sigma \Delta\lambda_{Ar}.U_{Ar} + \Sigma \Delta\lambda_{Bs}.U_{Bs}.$$

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[1] A suitable example is provided by the equation representing the Deacon process for manufacture of chlorine:

$$4\mathrm{HCl} + \mathrm{O_2} \rightleftarrows 2\mathrm{H_2O} + 2\mathrm{Cl_2}$$

i.e. 4 molecules of HCl and one molecule of oxygen react to form two molecules of water, and two of chlorine. We have

$$A_1 \equiv \mathrm{HCl}, \; a_1 = 4; \; A_2 \equiv \mathrm{O_2}, \; a_2 = 1$$
$$B_1 \equiv \mathrm{H_2O}, \; b_1 = 2; \; B_2 \equiv \mathrm{Cl_2}, \; b_2 = 2.$$

Now $\Delta\lambda_{Ar} = -a_r$, and $\Delta\lambda_{Bs} = b_{Bs}$, for a_r mols of A_r disappear and b_s mols of B_s appear after reaction. We have now

$$\Delta U = \Sigma b_s U_{Bs} - \Sigma a_r U_{Ar} \quad . \quad . \quad . \quad (4a)$$

Let Q_v be the heat evolved in the reaction which takes place at constant volume, as expressed by the symbolic formula

$$a_1A_1+a_2A_2+\dots a_rA_r+\dots = b_1B_1+b_2B_2+\dots b_sB_s+\dots+Q_v \quad . \quad . \quad (1a)$$

Hence, we have from the first law, since $p\,\Delta V=0$,

$$Q_v = -\Delta U = \Sigma a_r U_{Ar} - \Sigma b_s . U_{Bs}. \quad . \quad . \quad . \quad (4b)$$

Heat of Reaction Q_p at constant pressure.—Under these conditions, there is a change in volume ΔV, for the number of mols of gas in the reaction-vessel increases by

$$\Delta\lambda = \Sigma b_s - \Sigma a_r \,; \text{ hence } \Delta V/V = \Delta\lambda/\lambda.$$

The work done by the system in changing to the equilibrium volume $V+\Delta V$ is given by

$$p\,\Delta V = pV . \Delta\lambda/\lambda = \Delta\lambda . RT.$$

The heat evolved Q_p is less than Q_v by this amount i.e., we have

$$Q_p = Q_v - \Delta\lambda . RT. \quad . \quad . \quad . \quad (5a)$$

We can also write from the first law

$$Q_p = -\Delta U - p\,\Delta V = -\Delta(U+pV) = -\Delta H. \quad . \quad . \quad (5b)$$

where **H** is the Total Heat function $U+pV$, and H_{Ar} is the total heat function for one mol of the gas A_r.

As an illustration, let us take the reaction $H_2+\frac{1}{2}O_2=(H_2O)+Q_v$. Here $\Sigma a_r=3/2$, $\Sigma b_s=0$ since a liquid is formed whose volume is negligible. Hence for the reaction at 20°C, the heat of reaction Q_p at constant pressure is given by $Q_p=Q_v-\Delta\lambda . RT=Q_v+3/2\ RT$.

Variation of Heats of Reaction.—From (4b), we have

$$\frac{dQ_v}{dT} = \sum_r a_r \frac{dU_{Ar}}{dT} - \sum_s b_s \frac{dU_{Bs}}{dT} = \Sigma a_r C_{v,Ar} - \Sigma b_s C_{v,Bs} = -\Delta C_v \quad (6a)$$

We have $\partial Q_v/\partial V=0$ for the U's are independent of volume.

Similarly from (5b), we have

$$\frac{dQ_p}{dT} = \Sigma a_r \frac{dH_{Ar}}{dT} - \Sigma b_s \frac{dH_{Bs}}{dT} = \Sigma a_r C_{p,Ar} - \Sigma b_s C_{p,Bs} = -\Delta C_p. \quad (6b)$$

These are known as Kirchhoff's relations after their discoverer. Integrating we have

$$Q_v = Q_{v,0} - \int_0^T \Delta C_v . \, dT, \quad Q_p = Q_{p,0} - \int^T \Delta C_p . \, dT \quad . \quad . \quad (6c)$$

18·4. The Law of Mass Action.—Our knowledge of the laws of Chemical Reactions and chemical equilibria has a long story behind it. It was realized in very early period of human civilisation that certain substances have great 'Affinity' for each other, and react rapidly when placed in contact. Later, certain investigators, particularly Berthollet in France (1799) recognised from his experiments and observations that this was not the whole story; but the relative masses of the reacting substances played a significant part. He found that while in the laboratory, sodium carbonate and calcium chloride when brought together reacted to form calcium carbonate and sodium chloride the opposite kind of reaction appeared to be taking place on the shores of some Egyptian lakes, where sodium carbonate was found to be crystallising out. Berthollet ascribed this to the presence of large excesses of sodium chloride in the lake water. He carried out certain experiments in support of his view, and stated "The chemical activity of a substance depends on the force of its affinity, and upon the mass which is present in a given volume."

Though the importance of the statement was not immediately recognised, (in fact it met with some opposition), evidences in favour of the view began to accumulate as more experiments began to be carried out, particularly by Wilhelmy in Germany, and Harcourt and Esson in England. But it was left to Guldberg and Waage, two Norwegian scientists, to state the law correctly and in exact terms in 1867. The arguments were very simple.

They recognised that in order that a reaction of the type (1) takes place, a_1 particles of A_1, a_2 of A_2. . . . etc. should collectively collide at one point. All such collisions may not result in a reaction, but some certainly will. The velocity of the direct reaction will be given by

$$w_1 = k_1 \, x_{A_1}^{a_1} . x_{A_2}^{a_2} \, . \, . \, . \, .$$

Similarly the velocity of the back reaction (involving B's) is given by

$$w_2 = k_2 \, x_{B_1}^{b_1} . x_{B_2}^{b_2} \, . \, . \, .$$

In the equilibrium state, the two velocities must be equal, *i.e.*, $w_1 = w_2$. Therefore we get

$$\frac{x_{B_1}^{b_1} . x_{B_2}^{b_2} \ldots}{x_{A_1}^{a_1} . x_{A_2}^{a_2} \ldots} = \frac{k_1}{k_2} = \text{constant.} \quad . \quad . \quad . \quad (7)$$

The values of k_1 and k_2 cannot be obtained from thermodynamics; they depend upon a large number of other factors and external circumstances which are not yet fully understood. The velocity of chemical reactions is not a subject of study of the present chapter. We are concerned here only with the study of equilibrium conditions.

The application of thermodynamics to this problem was first made by Van't Hoff in 1877 by making use of semi-permeable membranes and reversible cycles. He discovered the differential laws of Reaction-Isobar (equation 17a), and Reaction Isochore (equation 17b), which are given in the next section.

In the following treatment we have followed W, Gibbs and Planck rather than van't Hoff, because the latter's method would have been a repetition of the procedure given in §6·10.

18·5. Laws of Chemical Reaction.

The Reaction-Isobar.—When the reaction takes place at constant pressure and constant temperature, the conditions of equilibrium are given by

$$\Delta \mathbf{G} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

where **G** is the Gibbs' function for the mixture. We have for the reaction (1), since p and T remain constant,

$$\begin{aligned} \Delta \mathbf{G} &= \Sigma \Delta\lambda_{Ar} . G_{Ar} + \Sigma \Delta\lambda_{Bs} . G_{Bs} \\ &= - \Sigma a_{Ar} G_{Ar} + \Sigma b_{Bs} G_{Bs} = 0. \quad . \quad . \quad (8b) \end{aligned}$$

G_{Ar} is the Gibbs' function for one mol of A_r in the mixture.[1]

Now $G = U + pV - TS = H - TS$. Hence using (5b), equation (8b) can be written as

$$\Sigma a_r S_{Ar} - \Sigma b_s S_{Bs} = \frac{1}{T} (\Sigma a_r H_{Ar} - \Sigma b_s H_{Bs}) = \frac{Q_p}{T}. \quad . \quad (9)$$

According to eqn. (27) p. 317, S_{Ar} is given by

$$S_{Ar} = C_{p,Ar} . \ln T - R \ln p_{Ar} + R \ln i_{Ar}$$

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[1] We ought to use the chemical potential $\mu_{Ar} = \partial \mathbf{G}/\partial\lambda_{Ar}$ in place of G_{Ar} as explained on p. 364, but since G_{Ar} is an extensive property for reactions at constant pressure we have $\mu_{Ar} = G_{Ar}$. We must however use the partial pressure p_{Ar} in evaluating G_{Ar} or S_{Ar} and not the total pressure p as explained on p. 317.

The value of 'i_{Ar}' is given in §11·21, p. 476, for monatomic gases. Let us now introduce two new symbols

$$\left.\begin{aligned} K_p &= \frac{\Pi\, p_{B_s}^{b_s}}{\Pi\, p_{A_r}^{a_r}} = \frac{p_{B_1}^{b_1} \cdot p_{B_2}^{b_2} \cdots}{p_{A_1}^{a_1} \cdot p_{A_2}^{a_2} \cdots} \\ \text{and} \qquad I &= \frac{\Pi\, i_{B_r}^{b_s}}{\Pi\, i_{A_r}^{a_r}} = \frac{i_{B_1}^{b_1} \cdot i_{B_2}^{b_3} \cdots}{i_{A_1}^{a_1} \quad i_{A_2}^{a_2} \cdots} \end{aligned}\right\} \quad . \quad . \quad . \quad (10)$$

Then (9) can be written as

$$ln\ K_p = \frac{Q_p}{RT} + \frac{ln\ T}{R} \cdot \Delta C_p + ln\ I. \quad . \qquad . \quad (11)$$

This is the equation of Reaction-Isobar.

The Reaction-Isochore.—When the reaction takes place under constant volume and constant temperature, the equilibrium is given by

$$\Delta \mathbf{F} = 0, \qquad . \quad . \quad . \quad . \quad . \quad . \quad (12a)$$

where **F** is the free energy of the mixture. Evidently for the reaction (1) under isothermal-isochoric conditions

$$\Delta \mathbf{F} = -\ \Sigma a_r\ \partial \mathbf{F}/\partial \lambda_{Ar} + \Sigma b_s\ \partial \mathbf{F}/\partial \lambda_{Bs} = 0. \quad . \qquad . \quad (12b)$$

Now $F = U - ST$, hence equation (12b), can be written as

$$\Sigma\, a_r\, \frac{\partial \mathrm{U}}{\partial \lambda_{Ar}} - \Sigma\, b_s\, \frac{\partial \mathrm{U}}{\partial \lambda_{Bs}} = T\left(\Sigma\, a_r\, \frac{\partial \mathrm{S}}{\partial \lambda_{Ar}} - \Sigma b_s\, \frac{\partial \mathrm{S}}{\partial \lambda_{Bs}}\right). \quad (13a)$$

Since U is an extensive property $\partial \mathrm{U}/\partial \lambda_{Ar} = U_{Ar}$, the internal energy of a gram-molecule of A_r. **S** for the mixture is from (27) p. 317 given by

$$\mathbf{S} = \Sigma \lambda_{Ar}\ [C_v\ ln\ T - \mathrm{R}\ ln \frac{\lambda_{Ar}\mathrm{R}}{V} + \mathrm{R}\ ln\ i]$$

$$\partial \mathrm{S}/\partial \lambda_{Ar} = C_{v,Ar}\ ln\ T - \mathrm{R}\ ln \frac{\lambda_{Ar}\mathrm{R}}{V} + \mathrm{R}\ ln\ i_{Ar}. \qquad (13b)$$

Putting $\lambda_{Ar} = x_{Ar}\, \lambda$, and introducing the symbol

$$K_x = \frac{\Pi\, x_{B_s}^{b_s}}{\Pi\, x_{Ar}^{a_r}} = \frac{x_{B_1}^{b_1} \cdot x_{B_2}^{b_2} \cdots}{x_{A_1}^{a_1} \cdot x_{A_2}^{a_2} \cdots} \qquad . \quad . \quad . \quad (14)$$

we can rewrite (13a) with the help of (13b), (14) and (4b) in the form[1]

$$\ln K_x = \frac{Q_v}{RT} + \frac{\ln T}{R}.\triangle C_v + \ln I + \triangle\lambda \ln \frac{V}{\lambda Re} \quad . \quad . \quad . \quad (15)$$

Equation (15) represents the law of Reaction Isochore.

Relation between the different equilibrium constants.—Since we have $p_{Ar} = x_{Ar}.p$, it can be easily shown that

$$K_p = K_x \times p^{\triangle\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16a)$$

Sometimes another quantity K_ν is used, which involves ν_{Ar} and ν_{Bs} i.e., mols per unit volume. We have

$$K_\nu = \frac{\prod \nu_{B_s}^{b}}{\prod \nu_{A_r}^{a_r}} = \frac{\nu_{B_1}^{b_1} \cdot \nu_{B_2}^{b_2} \cdots}{\nu_{A_1}^{a_1} \cdot \nu_{A_2}^{a_2} \cdots}$$

Since $p_{Ar} = \nu_{Ar}.RT$, it can be easily shown that

$$K_p = K_\nu\,(RT)^{\triangle\lambda}, \quad K_\nu = K_x.\ V^{-\triangle\lambda}. \quad . \quad . \quad . \quad .. \quad (16b)$$

From equations (16a) and (16b) we deduce that when $\triangle\lambda = 0$, i.e., a chemical reaction is not attended with a change in mol-number e.g., in the case $H_2 + I_2 \rightleftarrows 2HI$, we have

$$K_p = K_x = K_\nu.$$

These form the simplest kind of chemical reactions, and are discussed in §18·7.

Differential Forms of the Equations.—Equation (11) shows that K_p is a function of T alone, and is independent of p. With the aid of (11) and (6b) we have

$$\left(\frac{\partial \ln K_p}{\partial T}\right)_p = -\frac{Q_p}{RT^2}, \quad \left(\frac{\partial \ln K_p}{\partial p}\right)_T = 0, \quad \left(\frac{\partial \ln K_p}{\partial V}\right)_T = 0. \quad . \quad (17a)$$

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[1] Formulae (15) and (11) can also be easily obtained from statistical mechanics. For proof see Fowler and Guggenheim, *Statistical Thermodynamics* (1939) pp. 158—167.

The differential relations of K_x are rather more involved. With the aid of (15), we deduce that

$$\left(\frac{\partial\, ln\, K_x}{\partial T}\right)_v = -\frac{Q_v}{RT^2}, \quad \left(\frac{\partial\, ln\, K_x}{\partial V}\right)_T = \frac{\Delta\lambda}{V}, \quad . \quad (17b)$$

$$\left(\frac{\partial\, ln\, K_x}{\partial T}\right)_p = -\frac{Q_v}{RT^2} + \frac{\partial}{\partial T}\left(\Delta\lambda\, .\, ln\frac{T}{p}\right) = -\frac{Q_v - \Delta\lambda .\, RT}{RT^2} = -\frac{Q_p}{RT^2},$$

and

$$\left(\frac{\partial\, ln\, K_x}{\partial p}\right)_T = -\frac{\Delta\lambda}{p} . \quad . \quad . \quad . \quad . \quad (17c)$$

The differential equations satisfied by K_p are

$$\left(\frac{\partial\, ln\, K_p}{\partial p}\right)_T = \left(\frac{\partial\, ln\, K_p}{\partial V}\right)_T = 0,$$

and

$$\left(\frac{\partial\, ln\, K_p}{\partial T}\right)_p = -\frac{Q_p}{RT^2} - \frac{\Delta\lambda}{T} = -\frac{Q_v}{RT^2} . \quad . \quad . \quad (17d)$$

The integral forms of the reaction equations (11) and (15) can be easily deduced from each other.

18·6. General Observations.—The differential equations of chemical equilibria were first obtained by the early pioneers like Van't Hoff, Gibbs and others by means of various ingenious devices, and expressions for integral equations like (11) and (15) were obtained from these by using various approximating assumptions. This course is sometimes still followed in Text-books on Physical Chemistry. But modern developments have rendered these methods unnecessary, though they are instructive from a historical point of view.

The equations developed in the foregoing sections show that for finding out the course of a homogeneous chemical reaction over a range of temperature and pressure, we require a knowledge of the following physical quantities :—

(a) Specific Heats at constant volume and constant pressure of the constituents, from the lowest to the actual temperatures of the reaction. This subject has been treated in Chapters III and XVI.

(b) Value of the Chemical Constants of the constituents. This has also been treated in Chapters XI and XVII, for monatomic and diatomic gases, and can be further worked out for polyatomic gases.

(c) Heats of Reaction involved in the process, preferably, if possible, at absolute zero.

The Heats of Formation can be obtained from calorimetric measurements in some cases, but this is not always possible, e.g., in reactions of the type $I_2 = I + I - U$. In such cases, formerly the procedure was reversed, viz., the laws of reaction were utilized to find out heats of reaction. Within the last thirty years, thanks to the pioneering work of Franck and others, spectroscopic methods are being used for finding out Heats of Reaction with much more precision than could be obtained by older methods. Brief descriptions will be found in subsequent work, but for full description, other treatises or original reviews may be consulted.

Chemists generally use the law of Reaction-Isobar (eqn. 11 p. 785) for discussion of Chemical Reactions. The law of Reaction-Isochore (eqn. 15) is seldom used. Both the forms are generally unsuitable, except for the case of simpler reactions where the inner degrees of freedom are not excited. When the temperature is such that these degrees of freedom are excited, the equations become rather too difficult to manage. These cases are discussed later (§18·12). We now give some simple cases.

ILLUSTRATION OF CHEMICAL EQUILIBRIA.

18·7. Chemical Reactions without change in mol-number.—Such reactions include several important ones e.g., $H_2 + I_2 \rightleftarrows 2HI$, $H_2 + CO_2 \rightleftarrows H_2O + CO$ (Water Gas Reaction) and the nitric oxide reaction $N_2 + O_2 \rightleftarrows 2NO$. For these, as mentioned before, $K_p = K_x = K_c$ and are independent of total volume or pressure.

This was proved in the case of the HI-reaction by Lemoine. Let us fill up a bulb HI at the pressure p, and heat it to a high temperature. Then suppose a fraction x dissociates. We have

$$p_{H_2} = p_{I_2} = nx.kT, \quad p_{HI} = n(1-x).kT, \quad p = n(1+x)kT.$$

We have therefore

$$K_p = \frac{p_{H_2} p_{I_2}}{p^2_{HI}} = \frac{x^2}{(1-x)^2} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and is independent of p *i.e.*, the fraction dissociated will be independent of pressure and will only be a function of T. The results of Lemoine at 440°C. reproduced below confirm this.

p in atmos:	4·5	2·3	1·0	·5	·2
x (fraction decomposed)	·24	·225	·27	·25	·29

The fractions were determined by suddenly cooling the heated bulb, and freezing the equilibrium *i.e.*, the reaction velocity became so small, that the equilibrium proportions of H_2, I_2, HI were maintained unaltered. HI was dissolved in water and determined chemically, from which proportions of H_2 and I_2 were determined.

The experiment was repeated with greater care by Bodenstein[1] who showed that the walls of the glass bulb adsorb considerable amounts of HI gas which is therefore withdrawn from the reaction. The previous results were therefore not so good as could be expected. He adopted a somewhat different procedure. a mols of H_2 and b mols of I_2 were sealed in the glass bulb, which was then heated for a considerable time at a constant temperature. Let x mols of I_2 combine with x mols of H_2 to form $2x$ mols of HI. The mixture was then rapidly cooled, the equilibrium was frozen, and the amounts of HI and I_2 were determined separately by titration. Since

$$p_{H_2} V = (a-x) RT, \quad p_{I_2} V = (b-x)RT, \quad p_{HI} V = 2xRT,$$

we should have

$$K_p = \frac{4x^2}{(a-x)\,(b-x)} = \text{constant}, \quad . \quad . \quad . \quad (19)$$

in whatsoever way a and b may be varied. This is illustrated in the following table compiled from Bodenstein's results.[1]

Table 1.—*The* $H_2+I_2 \rightleftharpoons 2HI$ *equilibrium.*

T=717°K (Boiling point of Sulphur)				T=630°K (Boiling point of Mercury).			
a in c.c.	b in c.c.	x in c.c.	K_p	a in c.c.	b in c.c.	x in c.c.	K_p
8·10	2·94	2·82	50·2	6·63	2·59	2·49	59·5
7·92	5·30	4·75	51·1	6·22	5·71	4·77	66·8
8·07	9·27	6·74	53·6	6·41	10·40	5·94	67·3
8·12	14·44	7·47	48·8	6·41	26·22	6·27	66·2
8·02	27·53	7·77	48·9	6·21	23·18	6·08	64·2
7·89	33·10	7·70	49·2	6·51	22·29	6·35	63·2
		Mean value 50·3				Mean value 64·5	

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[1] *Zeits. f. phys. Chem.*, **29**, 295, 1899.

We thus find that K_p remains approximately constant at any particular temperature. From the value of K_p at two temperatures which are close to each other, it is possible to calculate the value of the Heat of Formation. We have

$$\frac{\partial \ln K_p}{\partial T} = -\frac{Q_p}{RT^2}.$$

Hence, supposing Q_p to be constant, we obtain after integration between the temperatures T_1 and T_2,

$$Q_p = \frac{RT_1T_2}{T_1 - T_2} \ln \frac{K_2}{K_1} \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

Taking $T_1 = 717^\circ$, $T_2 = 637^\circ$K, and the corresponding values of K_p, we obtain $Q_p = 2580$ cal., *i.e.*, 2580 calories of heat are evolved in the formation of two mols of HI out of one mol of H_2 and one mol of gaseous I_2.

The reaction $H_2 + [I_2] \rightleftarrows 2HI$ is endothermic, but this fact is not contrary to the result obtained here. We have

$$H_2 + I_2 = H_2 + [I_2] + L,$$

where L=heat of sublimation of iodine. Hence

$$H_2 + [I_2] = H_2 + I_2 - L = 2HI - L + Q_p.$$

Now $L = 10600$ cal. Hence $Q_p - L = -8020$ cal. or the reaction is endothermic.

18·8. Dissociation of a Complex Molecule into two identical simpler molecules.

18·8. Dissociation of a Complex Molecule into two identical simpler molecules.—This is afforded by N_2O_4 gas which even at ordinary temperatures is partially dissociated into NO_2. This is shown by the fact that at high pressures, the density is 46, showing that N_2O_4 is undissociated; as the pressure is lowered, the density becomes less and less, till at very low pressures, the density falls to 23, showing that N_2O_4 has been almost completely dissociated into NO_2. The dissociation can be explained with the help of law of Reaction Isobar.

Let n_0 = mol number of undissociated N_2O_4, and let a fraction x be decomposed into NO_2. Then at any instant, we have $n_0(1-x)$ mols of N_2O_4, $2xn$ mols of NO_2 and altogether $n_0(1+x)$ mols of gas. Hence

$$p_{N_2O_4} V = n_0(1-x)RT, \quad p_{NO_2} V = 2n_0 x RT, \quad pV = n_0(1+x)RT.$$

Therefore $x = \dfrac{pV}{n_0RT} - 1$ and the density $d = \dfrac{\rho}{1+x}$, . . (21)

ρ being the density of undissociated N_2O_4. Therefore $x = (\rho/d) - 1$. Studying the reaction as one of dissociation we have for the dissociation constant

$$K_p = p^2_{NO_2}/p_{N_2O_4} = \frac{4x^2}{1-x^2}p \doteq \text{const.} \quad . \quad . \quad (22)$$

The results are illustrated in Table 2.

Table 2.—Dissociation of N_2O_4 at 49·7°C. under varying pressure.

p (in mm.)	V (in litres)	$p \times V$	x(obs.) $\frac{pV}{n_0RT} - 1$	$K_p = \frac{4x^2}{1-x^2}p$ (p in atmos.)	x calc.
0	∞	4020	1	..	..
26·80	143·3	3840	0·910	0·160	0·917
93·75	38·2	3570	0·776	0·186	0·784
182·69	18·5	3380	0·680	0·209	0·673
261·37	12·4	3260	0·620	0·217	0·605
497·75	6·0	2990	0·485	0·190	0·483
∞	..	2010	..	..	..

Mean value of $K_p = 0·197$.

Thus N_2O_4 is almost completely dissociated into NO_2 even at ordinary temperature if the pressure be sufficiently low. With rise in pressure, the dissociation decreases. These results are evident from equation (22). The value of K_p is given in column 5, but K_p can hardly be said to be constant, as expected theoretically. This is ascribed to experimental errors, and to deviation of the constituents from the laws of perfect gases at higher pressures. Taking the mean value of K_p, we can calculate x as a function of pressure, according to the relation

$$\frac{4x^2}{1-x^2}p = K_p, \quad \text{or } x = f\left(\frac{K_p}{p}\right), \quad . \quad . \quad . \quad . \quad (23)$$

and can interpolate the value of x for any pressure. These are calculated in the sixth column. The departures from the values in the fourth column are not large. The shows that a large error in the value of K_p causes but a slight error in the value of x. The procedure, can be hardly justified[1].

18·9. Use of Laws of Chemical Reaction in synthesis of chemical compounds ; Synthesis of Ammonia (The Haber Process).—The Laws of Chemical Reaction serve as guides for the synthesis of many chemical compounds of great industrial value. The most famous case is that of synthetic ammonia, which was perfected by Haber just before the first world war, and played a great part in history.[1]

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[1] For electro-chemical method of determining HI-reaction, see Stegmüller, *Zeits. f. Electrochemie*, **16**, 85, 1910.

We shall study the reaction as one of formation, not of decomposition, *viz.*,

$$N_2+3H_2 \rightleftarrows 2NH_3 \qquad . \quad . \quad . \quad . \quad (24)$$

Let us confine three volumes of H_2 and one volume of N_2 in a space having the temperature T, pressure p, and let us suppose that x is the fraction of NH_3 produced to the whole molar contents. Then we have

$$p_{NH_3}=xp, \quad p_{N_2}=\tfrac{1}{4}(1-x)p, \quad p_{H_2}=\tfrac{3}{4}(1-x)p,$$

and hence

$$K_p=\frac{p^2_{NH_3}}{p_{N_2}p^3_{H_2}}=\frac{x^2}{(1-x)^4p^2}\,\frac{4^4}{3^3}=\text{constant.} \quad . \quad . \quad (25)$$

The important point to observe here is that at any fixed temperature x will increase with the increase of p. So compression is needed to get a good yield.

We describe here the apparatus of Larson and Dodge,[2] who investigated the reaction at pressures of 10, 30, 50, 100 and 1000 atmospheres between the temperature 350°C to 500°C.

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[1] We may briefly describe why the synthesis was considered to be of such great economic importance. The manufacture of nitric acid and the nitrates is one of the most important chemical industries in the world, as they form the starting point for the manufacture of explosives, fertilizers, and other chemicals. Before World War I, the world was dependent upon Chili for the supply of sodium nitrate. Attempts were made to prepare nitrate cheaply by other methods (e.g., by the Birkeland-Eyde process in Norway), but they could not compete successfully with the Chili nitrates. Oswald had discovered in 1900 that ammonia, on being sparked with atmospheric air in the presence of catalysers, easily converts into nitric acid but for this work pure ammonia must be used as otherwise the catalyser is poisoned (rendered unfit for use). Ammonia was usually obtained from coal-tar distillation and was impure and unsuitable for the Oswald process. So the need arose for a cheap method of manufacture of pure ammonia. Attempts to synthesise ammonia out of N_2 and H_2 were made by St. Claire Deville and Ramsay and Young, but they were unsuccessful. Things were at this stage when Haber took up the work. He saw from the application of the law of chemical action (aided by the extension known as Nernst's Heat Theorem) that the mixture must be compressed to a high pressure, and at the same time, the temperature must be sufficiently high in order that the velocity of reaction in presence of catalysers may be sufficiently great.

[2] *Jour. Amer. Chem. Soc.*, **45**, 2918, 1923; **46**, 367, 1924.

The apparatus consists of a strong spiral S of iron tube (Fig. 1) embedded in a bath of $NaNO_3$ and KNO_3. The bath is maintained at constant temperature by electrical heating and stirring. Iron tubes were selected because they were found not to be attacked by heated H_2 and N_2. The reaction took place within a bomb charged with some catalyst (Fe, Mn or Osmium). A mixture of N_2 and H_2 in the proportion of 1 : 3 was confined in gasometers under the desired pressure and allowed to pass through the spiral under varying velocities of flow. This was to see whether the reaction was independent of the velocity of flow. The gas issues out at 1 atmos. pressure, and rather low temperature, the equilibrium is therefore frozen out. The gas was analysed chemically for ammonia and the percentage of formation was determined. The results are shown in Table 3.

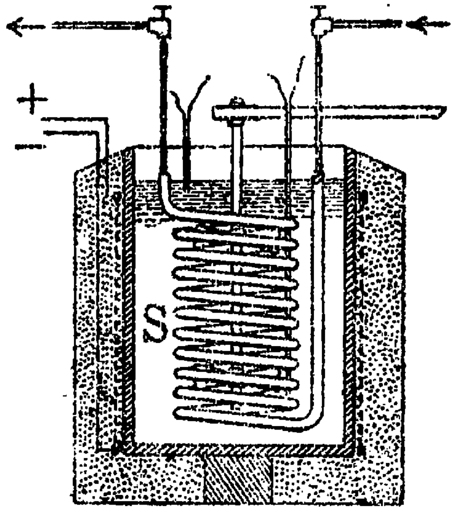

Fig. 1.– Apparatus of Larson and Dodge for studying the synthesis of ammonia.

Table 3.—Percentage synthesis of ammonia at different temperatures and pressures.

Temp. / pressure in atm.	350°C.	375°C.	400°C.	425°C.	450°C.	475°C.	500°C.
10	7·35 *·0266*	5·25 *·0181*	3·85 *·0129*	2·80 *·0092*	2·04 *·0066*	1·61 *·0052*	1·20 *·0038*
30	17·80 *·0273*	13·35 *·0184*	10·11 *·0129*	7·6 *·0092*	5·80 *·0068*	4·53 *·0052*	3·48 *·0038*
50	25·1 *·0278*	19·44 *·0186*	15·1 *·0130*	11·7 *·0093*	9·17 *·0069*	7·13 *·0051*	5·58 *·0039*
100		30·95 *·0202*	24·9 *·0137*	20:2 *·0099*	16·35 *·0072*	12·98 *·0053*	10·40 *·0040*
300					35·5 *·0088*	31·0 *·0067*	26·2 *·0050*
600					53·6 *·0129*	47·5 *·0089*	42·1 *·0065*
1000					69·4 *·0238*	63·5 *·0149*	

The values of x, and K_p are given on the left and right of each column. For example, at 400°C, and 30 Atm, $x=10\cdot 11$, $K_p=\cdot 0129$. It will be seen that the yield is highest at large pressures and lower temperatures. At such high pressures, the laws of perfect gases hardly hold.

18·10. Dissociation of Diatomic Molecules into Atoms. A review of experimental methods.

—A large number of commoner elements occur in Nature in the form of diatomic molecules, e.g., H_2, N_2, O_2, the halogens. With rise of temperature they are expected to dissociate into atoms, but the heat of dissociation is generally so large, that it becomes difficult to devise any direct experimental method for studying their dissociation equilibria. A few are described below.

(*a*) *Direct Thermodynamical Method.*—We describe, for the sake of illustration, Bodenstein and Starck's apparatus (Fig. 2) for the study of the decomposition of I_2 vapour.

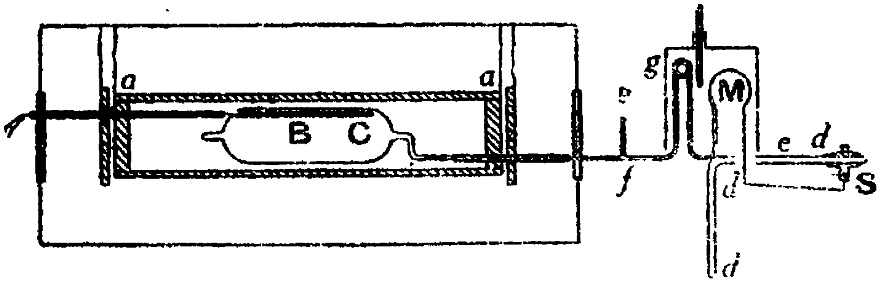

Fig. 2.—Bodenstein and Starck's apparatus for studying the dissociation of iodine.

'*aa*' is an electrical furnace of porcelain the middle part of which can be kept at a constant temperature correct up to 1°. B is a quartz vessel coated over with a platinum gauze to keep the temperature uniform; C is a Pt—Pt-Rh couple for measuring the temperature. B ends in a capillary tube connected to a quartz fibre manometer M for measuring the pressure of the enclosed gas.

The experiment is carried out as follows:—A known amount of I_2 is taken in a weighed quartz capsule, which is placed in B and sealed. Then B is evacuated and sealed off at P. The furnace is then heated to various temperatures, and every ten minutes T and p are observed. Then the vessel is cooled, the glass melted off at P, B washed with KCl-solution, the iodine is titrated with sodium thiosulphate and estimated. The volume of B is also determined. $V=249\cdot 3$ c.c., amount taken$=1\cdot 54\times 10^{-3}$ mole.

We have, as in the case of N_2O_4, $p_{I_2} = n(1-x).kT$, $p_I = 2x.nkT$, $p=n(1+x).kT$. So $x = \frac{p}{nkT} - 1$. The value of $K_p = \frac{4x^2}{1-x^2}p$. Bodenstein and Starck's values of K_p are shown in Table 4.

Table 4.—Experimental results on Dissociation of Iodine.

Temperature °K	Pressure in mm. of Hg	x	K_p
1073	435·6	0·068	0·0107
1173	503·6	0·128	0·0441
1273	590·3	0·219	0·1568
1373	694·5	0·340	0·4811
1473	820·7	0·460	1·2000

These experimental results have been compared with detailed theoretical calculations by Gibson and Heitler, and by Giauque and Overstreet. For details see §18·12.

(*b*) *The Effusion Method.*—This method was applied by de Vries and Rodebush[1] for studying the dissociation of I_2 and Br_2 and was extended by Bichowsky and Copeland[2] for studying the difficult problem of finding out the heat of dissociation of H_2, and by Wrede[3] for finding out the nature of active nitrogen. The principle underlying the method is as follows:—

We have seen on p. 193, Chap. III, that if there is a small orifice of area A in a vessel containing a gas of molecular weight M at pressure p_0 and temperature T_0, then, provided the dimensions of the orifice are small compared to the mean free path of the molecules, the rate of flow into a second vessel containing the same gas at a small negligible pressure p' is given by

$$m_0 = \tfrac{1}{4}A\rho_0\bar{c}_0,$$

where m_0 is the mass of gas flowing out per unit time,

$$\text{and} \quad \rho_0 = \frac{Mp_0}{RT_0}, \quad \bar{c}_0 = \sqrt{\frac{8RT_0}{M\pi}}. \quad \therefore m_0 = Ap_0\sqrt{\frac{M}{2\pi RT_0}} \quad . \qquad (26)$$

Suppose now the vessel is heated to $T°$ and a certain amount of the gas, which is diatomic, is decomposed into atoms. Then the partial pressure of the undecomposed gas is $p(1-x)/(1+x)$ and the molecular weight is M, while the partial pressure of decomposed gas is $2px/(1+x)$ and molecular weight is $M/2$, where p denotes the final total pressure. The mass w now flowing out of the orifices consists of both molecules and atoms. We have

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[1] *Jour. Amer. Chem. Soc.*, **49**, 656, 1927.
[2] *Jour. Amer. Chem. Soc.*, **50**, 1315, 1928.
[3] *Zeits. f. Physik*, **54**, 53, 1929.

$$w = \frac{A}{\sqrt{2\pi RT}}\left[p\,\frac{1-x}{1+x}\sqrt{M} + \frac{2px}{1+x}\sqrt{\frac{M}{2}}\right]. \qquad (27)$$

Let the time of flow be the same and let us compare the two masses. We have

$$\frac{w}{w_0} = \frac{p}{p_0}\sqrt{\frac{T_0}{T}}\left[\frac{1-x}{1+x} + \frac{x\sqrt{2}}{1+x}\right] \quad . \quad . \quad . \quad (28)$$

from which we deduce after simplification,

$$x = \frac{1-y}{y-\cdot 414}, \text{ where } y = \frac{w}{w_0}\sqrt{\frac{T}{T_0}}\cdot\frac{p_0}{p}.$$

x can be calculated at different temperatures and pressures, and the law of mass action may be verified. The value of the constant K_p as well as the heat of formation may be calculated.

The apparatus is shown in Fig. 2. It consists of a quartz tube T, 66 cm. in length and 2·4 cm. in diameter placed inside an electric furnace F. It is provided with a diaphragm, and a small hole at O. S is a reservoir for solid I_2 at 0°C, and ·030 mm. pressure. C is a thermocouple. The gas effusing out is collected at R which is cooled by means of liquid air. The space between O and R is evacuated by means of a high vacuum pump (10^{-5} mm. of Hg). The quantity of I_2 is estimated by dissolving it in KI-solution and titrating with sodium thiosulphate solution. Bromine may be treated in a similar way.

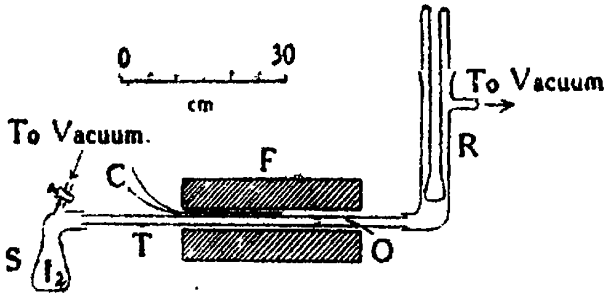

Fig. 3.—Apparatus for studying the dissociation of iodine.

Results obtained by this method, however, differ not inconsiderably with those obtained by Bodenstein. For discussion the original papers should be consulted.

(*c*) *Heat of Dissociation of Hydrogen.*—As hydrogen cannot be appreciably decomposed by the temperature usually available in laboratories, Bichowsky and Copeland produced atomic hydrogen by passing a steady condensed discharge through a low pressure hydrogen tube, as was first done by R. W. Wood. A mixture of atomic hydrogen produced in this way and molecular hydrogen was allowed to pass through the orifices into vacuum, and the degree of dissociation was determined by comparing the rates of flow of this mixture with that of pure H_2 gas. It amounted to as much as 29%. The outflowing atomic hydrogen was allowed to impinge on a platinum calorimeter, and recombine, the platinum surface acting as a catalyst. The total heat developed by recombination can be easily calculated from calorimetric measurements and knowing the amount of atomic hydrogen from the degree of dissociation, the heat of dissociation could be found.

The apparatus is shown in Fig. 4.

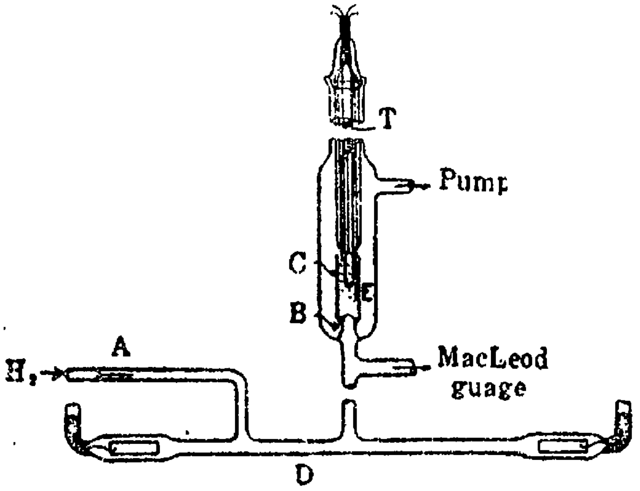

Fig. 4.—Apparatus of Bichowski and Copeland for finding the heat of dissociation of hydrogen.

Hydrogen flows steadily through the capillary A into the discharge tube D. The pressure is about ½ mm. and discharge is passed from a transformer (1000 volt, ·2 amp.). About 29% is atomised. The gas flows out through the orifices at B into the space E where a vacuum of ·005 mm. is maintained. C is the platinum-calorimeter provided with a Beckmann thermometer T. The space between the bulb of the Beckmann thermometer and the calorimeter is filled up with Wood's alloy. The calorimeter is calibrated by an insulated nichrome spiral embedded in Wood's metal.

The heat of dissociation D of H_2 obtained by this method is 106900 cal. and is estimated to be correct within 5%. The method has been further extended by Copeland to the case of oxygen who finds $D=131{\cdot}6$ k. cal. This seems to be an overestimate (*P.R.S.* **36**, 1221, 1930). The value of D obtained from spectroscopic measurements varies from 116 to 128 k. cal.

18·11. Combination of Several Equilibria. Calculation of a new Equilibrium from Measurement of other Equilibria.—The law of reaction isobar is very widely used to predict a new equilibrium out of two known equilibria. For illustration we take the two equilibria :—

$$2H_2O \rightleftarrows 2H_2+O_2, \qquad 2CO_2 \rightleftarrows 2CO+O_2.$$

Let us denote by K_{H_2O} the constant $\frac{p^2_{H_2}p_{O_2}}{p^2_{H_2O}}$ and by K_{CO_2} the constant $\frac{p^2_{CO}p_{O_2}}{p^2_{CO_2}}$. Dividing one by the other, we get

$$\frac{p_{H_2}\,p_{CO_2}}{p_{H_2O}\,p_{CO}} = \sqrt{\frac{K_{H_2O}}{K_{CO_2}}},$$

i.e., we deduce out of water and carbon-dioxide reactions the equilibrium constant of the water gas reaction

$$CO_2+H_2 \rightleftarrows H_2O+CO. \quad . \quad . \quad . \quad . \quad . \quad (29)$$

It is found that at 1396°C and atmospheric pressure, $K_{CO_2}=1{\cdot}34\times10^{-14}$ corresponding to a dissociation of $1{\cdot}44\times10^{-4}$ obtained by the streaming method. K_{H_2O} is extrapolated to be $\cdot25\times10^{-14}$. The K for water gas reaction is calculated to be 2·28, while direct experiments by Neumann and Köhler gave $K=2{\cdot}5$.

Other complicated reactions can be reduced to simpler reactions in a similar way.

For example, the Deacon process which is used for the manufacture of chlorine from HCl according to the formula

$$4HCl+O_2 \rightleftarrows 2H_2O+2Cl_2 \quad . \quad . \quad (30)$$

can be resolved into the two reactions

$$2HCl \rightleftarrows H_2+Cl_2, \quad 2H_2O \rightleftarrows 2H_2+O_2$$

Thus, $K_D=K^2_{HCl}/K_{H_2O}$.

The device can also be used in a reverse way, for it is comparatively easy to determine the equilibrium in Deacon's process as it is about half accomplished below 1000°C. But at these temperatures HCl, and still more H_2O, are but slightly decomposed. We can therefore deduce K_{H_2O} from known values of K_D and K_{HCl}.

18·12. Laws of Chemical Reaction in terms of Partition functions.

There is a tendency now to use 'partition functions' directly for discussion of complex cases of chemical equilibria like that of I_2-decomposition discussed in §18·10. We give a short account of these methods with a few illustrations.

From equation (68) p. 766 we have for the temperature-dependent part of Gibbs' function

$$G_T = (U+pV-TS)_T = -RT\,ln\,(f_t\,F_r\,F_v\,F_e\,\ldots)$$

since $pV = \frac{2}{3}U_T$, so that we can write generally

$$G = G_0 + G_T = U_0 - RT\,ln\,(f_t\,F_r\,F_v\,F_e\,..), \qquad (31)$$

for $G_0 = (U+pV-TS)_0 = U_0$ = internal energy of the constituent at absolute zero. We are neglecting the partition function for the nuclear spin, as in all chemical reactions not involving hydrogen this cancels out.

Now from the condition $\Delta G = 0$, as in §18·5, we have

$$\Sigma\, b_s\{U_0 - RT\,ln\,(f_t\,F_r\,F_v\,F_e)\}_{B_s}$$
$$-\Sigma\, a_r\{U_0 - RT.\,ln\,(f_t\,F_r\,F_v\,F_e)\}_{A_r} = 0. \qquad (32)$$

Now from equation (18), p. 750 we have

$$f_t = \frac{(2\pi mkT)^{3/2}}{nh^3} = \frac{(2\pi m)^{3/2}k^{5/2}}{h^3}\cdot\frac{T^{5/2}}{p} = i_t.\frac{T^{5/2}}{p},$$

so that $$ln\,f_t = \frac{5}{2}\,ln\,T - ln\,p + ln\,i_t,$$

where $$i_t = (2\pi m)^{3/2}\,k^{5/2}/h^3\,,$$

and p denotes the partial pressure.

Further as in equation (4b) p. 782, we have

$$\Sigma\, b_s\,(U_0)_{Bs} - \Sigma\, a_r\,(U_0)_{Ar} = -Q_v{}^0.$$

Hence we have rewriting (32),

$$ln\,K_p = \frac{Q_v{}^0}{RT} + \frac{5}{2}\Delta\lambda.\,ln\,T + ln\,I_t + ln\,F. \qquad (33)$$

where I_t is defined in §18·5, and F is given by

$$F = \frac{\prod_{Bs}(F_r\,F_v\,F_e\ldots)^{b_s}}{\prod_{Ar}(F_r\,F_v\,F_e\,..)^{a_r}}. \qquad (34)$$

As an illustration of (34), we calculate a formula for the dissociation of I_2. The process is

$$I_2 = 2I - D. \qquad (35)$$

Value of $Q_v{}^0$: It is easily seen that $-Q_v{}^0$ is the heat of dissociation of I_2 at absolute zero. It can be calculated very easily from spectroscopic data.

Iodine vapour shows a band absorption which passes into continuous absorption at $\lambda=4995$ Å. U. The band-absorption is due to electron excitation of I_2-molecule, and Franck showed that the beginning of continuous absorption marks the dissociation of I_2 into a normal and an excited iodine atom according to the formula

$$I_2+h\nu = I(^2P_{3/2}) + I(^2P_{1/2}).$$

$^2P_{3/2}$ is the normal state of I-atom, $^2P_{1/2}$ is the excited state, and from spectroscopy, we know that $^2P_{3/2}-{}^2P_{1/2}$ of I=7600 cm^{-1}. Hence $Nh\nu=D+Nh\,(^2P_{3/2}-{}^2P_{1/2})$. This gives $D=35{\cdot}40$ K. cal.

For the reaction (35) we have $b_r=2$, $a_r=1$, $\triangle\lambda=1$. Now let us calculate F. (F_r F_v $F_e\ldots$) for I_2, which occurs in the denominator can be obtained from the spectral knowledge of I_2.

We have $B={\cdot}373-{\cdot}00012\,v$ cm^{-1} and it is so small that all the rotational states are excited. We have therefore from eqn. (70), p. 767

$$F_r = 4\pi^2 I.kT/h^2.$$

$F_v=(1-e^{-h\nu/kT})^{-1}$ as given on p. 767 eqn. (72), and ν from spectroscopic analysis = 213·76 cm^{-1}.

F_e for $I_2=1$, for the fundamental electronic term is $^1\Sigma_0$. F_e for I is equal to $4+2\,e^{-h\nu/kT}+\ldots\cong 4$, for the fundamental term of I which is $^2P_{3/2}$ has the weight 4. If the temperature is high enough for the excitation of the metastable state $^2P_{1/2}$, we have for the second term $\nu={}^2P_{3/2}-{}^2P_{1/2}\cong 7{,}600$ cm^{-1}. The nuclear spin terms for the atom and the molecule will cancel out. We have

$$I_t=\left\{\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}\right\}^2\Bigg/\frac{(2\pi.2m)^{3/2}k^{5/2}}{h^3} = (\pi m)^{3/2}k^{5/2}/h^3.$$

Collecting the terms, we have

$$ln\,K_p = -\frac{D}{RT}+\frac{3}{2}\,ln\left(\frac{\pi mkT}{h^2}\right)-ln\,\frac{8\pi^2 I}{h^2}+ln\,(1-e^{-h\nu/kT})$$
$$+\,ln\,2+2\,ln\,4. \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

2 in *ln* 2 is the symmetry number for this molecule and arises from the fact there are two identical atoms in the molecule.

The theoretical calculation of the quantity K_p by using formula (36) was given by Gibson and Heitler[1] and later more accurately by Giauque and Overstreet, whose calculations are given in Table 5.

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[1] Gibson and Heitler, *Zs. f. Phys.*, **49**; Giauque and Overstreet *Jour. Am. Chem. Soc.*, **54**; see Zeise, *Zeits. f. Elektrochem.*, **39**, 758, 895, (1933); **40**, 662, 885 (1934).

Their results are compared with the experimental values of Bodenstein and Starck in Fig. 5.

Table 5.—*Values of the equilibrium constant by calculation.*

T	K_p	$x = \sqrt{K/(4p+K)}$ %
400	$4{\cdot}26 \times 10^{-15}$	$3{\cdot}26 \times 10^{-6}$
600	$1{\cdot}63 \times 10^{-8}$	$6{\cdot}39 \times 10^{-3}$
800	$3{\cdot}24 \times 10^{-5}$	0·285
1000	$3{\cdot}32 \times 10^{-3}$	2·88
1200	$7{\cdot}22 \times 10^{-2}$	13·32
1400	$6{\cdot}54 \times 10^{-1}$	37·49
1600	3·48	68·21
1800	12·87	93·03
2000	36·60	94·95

For the other halogens the calculation is more complicated because they are made up of isotopes in varying proportions, though the physical constants needed are accurately known. For details see Zeise, ***loc. cit.*** For calculation of the dissociation equilibria of other molecules, special papers may be consulted.

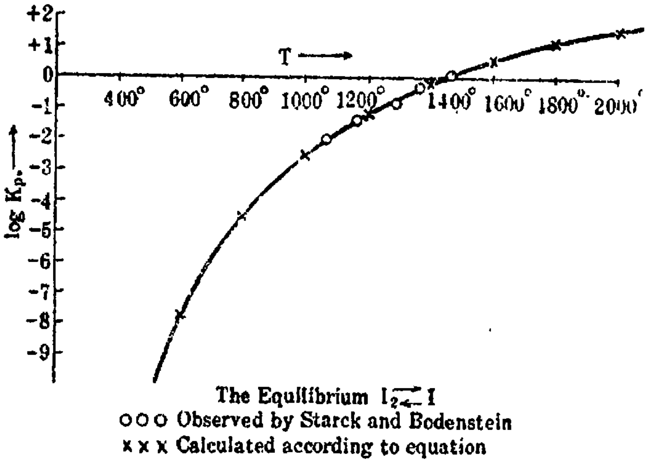

Fig. 5.—K_p at different temperatures.

18·13. The Le Chatelier-Braun Principle.—This principle may be stated as follows :—If any one of the variable factors determining the condition of equilibrium changes, the equilibrium shifts itself in such a way as to tend to annul the effect of that change. For example, if the temperature of the system is increased, other factors remaining constant, the equilibrium will change in such a direction as will involve an absorption of heat. Similarly if the pressure on the system is increased the equilibrium changes itself in that direction in which the volume occupied by the system will decrease. Again if the concentration of one of the components of the system is increased, the equilibrium will so change itself that the concentration of that particular component would tend to decrease. It can be easily verified that these requirements of the Le Chatelier-Braun principle follow from the differential laws of reaction-isobar and reaction-isochore. For example from (17b) we see that if Q_v is positive, i.e., the reaction proceeds towards the right with evolution of heat, $\partial(ln\ K_x)/\partial T$ is negative. Therefore for positive values of dT, i.e., for an increase in temperature K_x decreases, i.e., the reaction is pushed in the backward direction which involves an absorption of heat.

18·14. Chemical Affinity.—The student must have been familiar with the term "Affinity" as used in descriptive chemistry. Two substances like H_2 and Cl_2 are said to possess affinity for each other because they readily combine to form HCl, when brought into contact with each other. We try to form a mechanical picture of the case by supposing that forces of attraction are developed between molecules of H_2 and Cl_2 when they are brought together, like that between two particles of matter, or between two atoms charged with different kinds of electricity. But a little consideration shows that the question is much more complex. The formation of HCl depends not only upon the coming together of H_2 and Cl_2 molecules, but also the ease with which H_2 molecules and Cl_2 molecules can be dissociated into atoms under the influence of the new forces coming into operation. Affinity apparently changes greatly with external circumstances, *viz.*, temperature and pressure, for it is a matter of common experience that substances which combine readily at low temperatures may refuse to combine at high temperatures. The problem is therefore not merely mechanical, but also largely statistical and can only be solved from precise thermodynamical considerations.

The earlier attempts to define affinity were largely mechanical, witness for example the crude ideas about chemical valency. Thomsen and Berthelot observed that in general, substances combine readily if their combination results in a large evolution of heat. Accordingly Berthelot proposed that the heat of reaction should be taken as a measure of the force which urges the reacting substances to the new condition. But this conception is erroneous, as according to it, every exothermic reaction should proceed to completion, and no reaction would be possible in which heat is absorbed (endothermic).

If we take H_2, O_2 and H_2O, each at one atmos. pressure and 2000°C., more H_2O is formed. But if the pressure of H_2 and O_2 be reduced to 1/1000 atmos., while the pressure of H_2O remains unchanged, H_2O will be further dissociated. The reaction becomes reversed in spite of the fact that heat is evolved in the combination of H_2 and O_2. This illustrates that a large heat of evolution does not always lead to formation of the compound.

Van't Hoff taught us how it is possible to obtain a precise measure of 'Affinity' from the second law of thermodynamics. *He showed that 'Affinity' may be measured by the maximum work which can be obtained from the heat evolved in the reaction.*

Take for example the reaction

$$2CO_2 \rightleftarrows 2CO + O_2.$$

Let us calculate the maximum amount of work to which the heat evolved in the combination of two mols of CO and one mol of O_2 into two mols of CO_2 can be converted. The heat of formation at 15°C. has been found to be 136000 cal. The maximum work available will evidently depend upon the temperature and the partial pressures of the reactants, and the process of conversion of heat to work must be carried out in a reversible way. Let us suppose that we have a very large reservoir containing the three gases at the partial pressures P_{CO_2}, P_{CO}, P_{O_2} at the temperature T. Let us also have another large chamber at the same temperature containing the same gases at the equilibrium pressures p_{CO_2}, p_{CO}, p_{O_2} so that $p^2_{CO_2}/p^2_{CO}\, p_{O_2}$ = constant. Then we can carry out the following imaginary process. The gases in chamber (1) may be separated by semipermeable membranes into three equal volumes having the pressures P_{CO_2}, P_{CO}, P_{O_2} as described on p. 317. No work is done in this process. Then we may take $2dn$ mols of CO, and dn mols of O_2 separately and convert them isothermally (by compression or rarefaction as the case may be) to the equilibrium pressures p_{CO} and p_{O_2}. The work in these processes are respectively

$$2dn.\ RT\ ln\ \frac{P_{CO}}{p_{CO}} \quad \text{and} \quad dn.\ RT\ ln\ \frac{P_{O_2}}{p_{O_2}}\ .$$

These two gases may now be led to the equilibrium chamber. No work is done as the partial pressures are the same and the equilibrium is not disturbed as there are large excesses of the gas. We may suppose that $2dn$ mols of CO and dn mols of O_2 combine to form $2dn$ mols of CO_2 at the pressure p_{CO_2}. Then the slight excess of $2dn$ mols may be removed by semipermeable membranes and converted by an isothermal expansion or contraction to the pressure P_{CO_2}. The work done in this process is equal to

$$-2dn.\ RT.\ ln\ \frac{P_{CO_2}}{p_{CO_2}}\ .$$

The excess CO_2 can now be introduced into the CO_2-chamber at pressure P_{CO_2}.

The net result is that we have formed $2dn$ mols of CO_2 out of $2dn$ mols of CO, and dn mols of O_2 without leaving any change in any system, and gained the work

$$dA = -\ dn\ RT\left[ln\ \frac{P^2_{CO_2}}{P^2_{CO}\cdot P_{O_2}} - ln\ \frac{p^2_{CO_2}}{p^2_{CO}\cdot p_{O_2}}\right].$$

Every stage in the process has been carried out in a reversible way, hence the work obtained is the maximum. When $dn=1$ we can take the work as a measure of the *Affinity* A. Therefore

$$A = -\ RT\left[ln\ \frac{P^2_{CO_2}}{P^2_{CO}\ P_{O_2}} - ln\ \frac{p^2_{CO_2}}{p^2_{CO}\cdot p_{O_2}}\right]\ .\quad .\quad (37)$$

It is quite clear that if the gases are already in the equilibrium condition, $A=0$ from (37), as is also apparent from the fact that the gases will show no further tendency to combine.

We shall illustrate equation (37) by an example. Let us take gases CO_2 and CO at partial pressures of one atmosphere and at $T=$ 1000°K. The affinity

$$A_0 = RT\,ln\ \frac{p^2_{CO_2}}{p^2_{CO}\,p_{O_2}} = -\ RT\ ln\ K_p\quad .\quad .\quad .\ (38)$$

if the equilibrium pressures are expressed in atmospheres. Thus at 1000°K, we have

$$A_0 = -\ RT\,ln\ K_p = 1{\cdot}987\times1000\times2{\cdot}30\times20{\cdot}03 = 90{,}000\ \text{cal. approx.}$$

i.e., when 2 mols of CO_2 are formed out of two mols of CO and one mol O_2 at 1000°K. and one atmosphere pressure, the maximum work available from the heat evolved is 90,000 cal. though the heat evolved is about 130,000 cal.

If we take $P_{CO_2} = 10^{-3}$ atmos. $P_{CO} = 1$ atmos. and $P_{O_2} = 10$ atmos., we get

$$A = 90{,}000\ \text{cal.} - RT\ ln\ \frac{(10^{-3})^2}{10} = 122{,}000\ \text{cal.}$$

i.e., the tendency to form CO_2 is much more increased. We now give below a table of values of A under different temperatures when the initial pressures for all the constituents are one atmosphere.

Table 6.—Calculation of affinity from the equilibrium constant.

Temp.	1000	1500	2000	2500	3000
$ln\ K_p$	20·03	10·25	5·36	2·44	·50
A in kilo. cal.	90	70	48·9	27·9	6·85

It is found that A approaches U asymptotically only at low temperatures. This is also apparent from the relation

$$A - T\frac{dA}{dT} = Q_p.$$

The affinity for chemical reactions can also be calculated from reversible cells, as explained in §8·6 for the Daniell cell, and the Clark cell. As a matter of fact, the electromotive force E is a direct measure of the affinity, and we have

$$E = \frac{A}{n\,.\,23000}$$

and

$$E - T\frac{dE}{dT} = \frac{Q_p}{n\,.\,23000},$$

where Q_p =heat of reaction, n=valency.

For further information the reader may consult *Fundamentals of Physical Chemistry* by Eucken, Jette and Lamer, or *Lehrbuch der Chemischen Physik* by Eucken.

18·15. Heterogeneous Equilibria.—We have so far considered the application of thermodynamics to homogeneous equilibria *i.e.*, all the reactants being in the gaseous phase. We shall now show how thermodynamical considerations can be extended to cases, when one or more of the reacting bodies is in a condensed phase. As a typical case we take the dissociation of calcium carbonate according to the equation $CaCO_3 \rightleftarrows CaO+CO_2$. Here $CaCO_3$ and CaO are solid, only CO_2 is gaseous. Now every solid, like a liquid, has a definite vapour pressure at a particular temperature, and this increases rapidly with temperature. The pressure may be extremely minute, still we can suppose it to be existing. Hence the reaction space contains [$CaCO_3$] and [CaO] in equilibrium with their vapour, and CO_2 gas.

We can suppose that the law of mass action holds for all reactants in the gaseous phase. We have then

$$\frac{p_{\mathrm{CaO}}\, p_{\mathrm{CO_2}}}{p_{\mathrm{CaCO_3}}} = K. \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

But p_{CaO} and $p_{\mathrm{CaCO_3}}$, are fixed for a given temperature, as they correspond to the vapour pressure of the two solid phases. Hence

$$p_{\mathrm{CO_2}} = K \frac{p_{\mathrm{CaCO_3}}}{p_{\mathrm{CaO}}} = K'. \quad . \quad . \quad . \quad . \quad . \quad (39a)$$

Accordingly, at a given temperature, calcium carbonate produces a perfectly definite vapour pressure of CO_2 which is known as the *dissociation pressure*. If solid $CaCO_3$ is taken in a closed vessel and heated, it will go on dissociating and giving up CO_2 as long as the partial pressure of CO_2 does not reach the equilibrium value. When this value is reached, decomposition will stop and no further lime will be produced. If CO_2 is removed as soon as it is formed by a current of air, $CaCO_3$ will go on decomposing. We give below Table 7 containing the dissociation pressure of $CaCO_3$ at different temperatures. Further figures for other carbonates will be found in Landolt and Bornstein's Tables, p. 1446 (1923 edition).

Table 7.—Dissociation Pressure of $CaCO_3$

Temperature in °K	787	865	1006	1073	1123	1181
Pressure in mm. of Hg	·29	2·63	52	192	374	760

The dissociation pressure is thus analogous to the vapour pressure of condensed phases and is entirely independent of the amount of matter in the condensed phases.

The evolution of CO_2 from heated $CaCO_3$ forms the simplest example (monovariant) of a *heterogeneous equilibrium*. Here, as in the case of vaporisation, the number of components is one, the number of phases is two (solid and gas), hence the number of degrees of freedom is one. If an excess of one of the solid products of decomposition say CaO, be present, the number of components increases by one, but the number of phases also increases by one (solid CaO) and hence the number of degrees of freedom remains unaltered. But we may have more complicated cases of heterogeneous equilibrium to deal with, *e.g.* in the reactions:

$$\mathrm{Fe+H_2O \rightleftarrows FeO+H_2} \quad . \quad . \quad . \quad . \quad . \quad (40a)$$

and

$$\mathrm{PbS+H_2 \rightleftarrows Pb+H_2S.} \quad . \quad . \quad . \quad . \quad . \quad (40b)$$

By an extension of the arguments given in §18·11 we obtain for (40a)

$$\frac{p_{\mathrm{FeO}}\ p_{\mathrm{H_2}}}{p_{\mathrm{Fe}}\ p_{\mathrm{H_2O}}} = \text{constant.}$$

But the concentrations of Fe and FeO vapours are fixed as they are in equilibrium with their solid phases. We have therefore

$$p_{\mathrm{H_2}}/p_{\mathrm{H_2O}} = \text{constant.} \quad . \quad . \quad . \quad (41)$$

Equation (41) was verified by G. Preuner at 900°C., who found that the ratio $p_{\mathrm{H_2}}/p_{\mathrm{H_2O}}$ remained constant within experimental errors even when the partial pressure of water vapour was increased by about five times. Table 8 shows his results.

Table 8.—*Dissociation of* H_2O.

$p_{\mathrm{H_2O}}$ in mm. of Hg	8·8	9·9	11·5	12·9	17·4	21·5	35·4	49·3
$p_{\mathrm{H_2}}$	6·1	7·0	7·5	9·2	11·3	15·0	23·0	32·0
$K=p_{\mathrm{H_2}}/p_{\mathrm{H_2O}}$	·69	·71	·65	·71	·65	·70	·65	·65

This is an illustration of a divariant system, for $C=3$, $P=3$ (solid Fe, solid FeO, gas), hence $F=2$. The number of independent components is three, because though there are four substances, they are connected by one relation. The two independent degrees of freedom are the temperature and pressure of one of the gaseous phases. The pressure of the other phase is automatically fixed.

For other cases of heterogeneous equilibria and experimental methods of studying them the student may consult Jellinek, *loc. cit.*, pp. 160-187.

REACTIONS AT HIGH TEMPERATURES

18·16.—Thermal Ionisation of Gases.—The methods which have been evolved in this chapter can easily be applied to the case of ionisation of gases by thermal excitation, the theory of which was first given by the senior author of this book in

1921. The subject can be introduced in the following way. The effect of heat on matter is to cause a general loosening of its component parts. At the lowest temperatures all substances exist in the solid state; when sufficient heat is added they pass to the liquid state (Fusion); at still higher temperatures, the liquid passes to the vapour state consisting of discrete molecules (Vaporisation). When the vapour is further heated, the molecules break up into atoms. The steps we have indicated may not follow in the order indicated, e.g., a solid may pass directly to the vapour state, without passing through the intermediate liquid state, but that is of no particular significance. The general sequence is as described above. "The next question is what happens when we heat a gaseous mass consisting of atoms to very high temperatures?"

It is to be expected that at very high temperatures the atoms will come into violent collisions with each other, and as a result, their valency electrons (electrons in the outermost layers) will either switch on to higher quantum orbits, or will be altogether knocked off. Vice versa, when an ionised atom and electron come together, the ion may capture the electron, and become a normal or an excited atom. The process is just analogous to chemical reactions sketched in the present chapter. Taking an element M, we may indicate the process of ionisation, and capture of electron by the ion by the typical form $\rightleftarrows$ for reversible chemical reactions:

$$M,\ M^{exc} \rightleftarrows M^{+} + e, \quad \text{(Ionisation and Recapture)}$$

where M^{+} denotes the ion and e the electron, both considered as gaseous.

The energy relation is given by

$$M \rightleftarrows M^{+} + e - U. \quad . \quad . \quad . \quad . \quad . \quad (42)$$

U is called the heat of ionisation. This most important quantity can now be determined for almost all elements, with great accuracy, from spectroscopic data. We illustrate the process by taking the typical case of the element sodium. The 'luminescent' states are given by

$$M^{+} + e = M^{exc} + h\nu$$

or

$$M^{+} + e = M^{norm} + h\nu. \quad . \quad . \quad . \quad . \quad (43)$$

The electron constitution of Na is $1s^2.\ 2s^2.\ 2p^6.\ 3s$, as shown in Fig. 6, and normally the valency electron is in the level $3s$. When it is excited the outermost electron jumps to higher states as indicated in Fig. 6, and we get a number of excited states np, $n=3, 4, 5..$ and others. These states are unstable, and as the electron jumps back to $3s$, we get the emission of lines of principal series $3s\ {}^2S_{\frac{1}{2}} - np\ {}^2P_{\frac{1}{2},\frac{3}{2}}$, $n=3, 4, 5, \ldots\ldots$, of which the first two are the well known yellow lines $\lambda = 5896$, 5890, and others form the higher members of the principal series. We can also excite the atom of Na by exposing it to light (photo-excitation). When Na-vapour is illuminated by continuous light, and the emergent light is examined by a spectroscope, the spectrum is found crossed by dark lines, which all form the principal series corresponding to the process $3s \rightarrow np$ and these lines ultimately run together, and come to a limit corresponding to $n=\infty$ and after that we have continuous absorption. This *Photo-electric Ionisation* can be represented by the formula

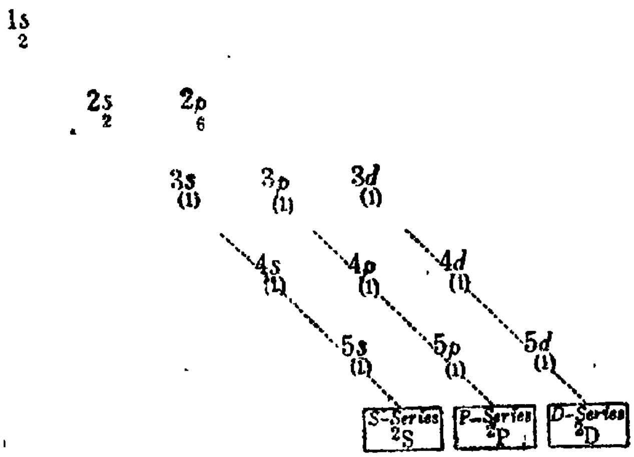

Fig. 6.—Structure diagram of Na.

$$\mathrm{Na}(3s) + h\nu = \mathrm{Na}^+ + e + \tfrac{1}{2}mv^2.$$

If $\nu > \nu_k$, ν_k being the limiting frequency where continuous absorption begins, the energy of the electron $= h(\nu - \nu_k) = \frac{1}{2}mv^2$. ν_k/c can be obtained experimentally, and for Na it is 41,000 cm^{-1}. We have

$$h\nu_k = e\chi/300, \qquad U = Nh\nu_k/J = \frac{N}{J}\cdot\frac{e\chi}{300}, \qquad (44)$$

where χ is the Ionisation Potential in volts. It can be easily shown that

$$U \text{ in calories} = \chi \text{ in volts} \times 23040 = \nu_k/c \text{ cm}^{-1} \times 2{\cdot}844. \qquad (45)$$

The excitation potentials.—The energy required to excite the electron from its normal state to any excited state can be expressed in terms of excitation potential. We have

$$h\nu_s = e\chi_s/300,$$

where $h\nu_s$, measures the excess energy possessed by the excited state, over that of the normal state e.g., for the sodium atom, if we take the *p*-states, (electronic level, *np*), ν_s/c is given by the terms $3^2S_{\frac{1}{2}}$—$3^2P_{\frac{1}{2},\frac{3}{2}}$, i.e., it is the inverse of the wavelength of the D_1, D_2-lines. For the 3*p*-states, ν_s/c has the values $10^8/5896=16956$ and $10^8/5890=16973$ and the excitation voltages for the two *p*-states, $3p\ ^2P_{\frac{1}{2}}$, $^2P_{\frac{3}{2}}$ are 16973/8102 and 16956/8102 i.e. about 2·09 volts. For fuller details about electron-constitution of atoms, and their different states, normal, metastable and excited, see *Treatise on Modern Physics* by Saha and Saha, Chap. XII.

Let us now suppose that the process (42) takes place at pressure p and temperature T. The amount of ionisation can be easily deduced from (33), by assuming the electron to be a gas of atomic weight $m=m_H/1836$ and applying the law of reaction-isobar. Equation (33) yields

$$\ln K_p = \frac{Q_v^0}{RT} + \frac{5}{2} \ln T + \ln I_t + \ln F \quad . \quad . \quad (46)$$

Now we have

$$K_p = p_{M^+} . p_e/p_M, \quad Q_v^0 = -U, \quad I_t = i_{M^+} . i_e/i_M = i_e = \frac{(2\pi m)^{3/2} k^{5/2}}{h^8},$$

$$F = g_e F_e(M^+)/F_e(M),$$

where $F_e(M)$ is the electronic partition function of the element M, $F_e(M^+)$ that of the ion, g_e is the weight factor of the electron and is equal to 2. We have now the equation of Thermal Ionisation

$$\ln \frac{p_{M^+} . p_e}{p_M} = -\frac{U}{RT} + \frac{5}{2} \ln T + \ln \frac{(2\pi m_e)^{3/2} k^{5/2}}{h^3} + \ln \left\{ 2 . \frac{F_e(M^+)}{F_e(M)} \right\} . \quad (47)$$

First approximation :

If we suppose that we had originally started with M and gone on heating it in a confined space to a temperature T, and x was the fraction ionised, we would have

$$p_e = p_{M+} = nxkT, \quad p_M = n(1-x)kT, \quad p = n(1+x)kT,$$

$$p_e = p_{M^+} = \frac{x}{1+x} p, \; p_M = \frac{1-x}{1+x} p,$$

for $p =$ total pressure $= p_e + p_{M^+} + p_M = n(1+x)kT$. If we ignore the last term of (47), we get

$$\log \frac{x^2}{1-x^2} p = -\frac{U}{2{\cdot}3RT} + \frac{5}{2}\log T - 6{\cdot}459, \quad . \quad . \quad (48)$$

where p is now expressed in atmospheres. This was the form in which the equation was originally given by the senior author in 1919.

Table 6.—*Percentage Ionisation of Calcium.*

pressure Temp.	1 atmos.	10^{-2} atmos.	10^{-4} atmos.
2000°K	..	..	$1{\cdot}4\times10^{-3}$
3000	..	..	1
4000		2·8	26
5000	2	20	90
6000	8	64	99
7000	23	91	100
8000	46	98·5	"
9000	70	100	"
10000	85	"	"
11000	93	"	"
12000	96·5	"	"
13000	98	"	"

As equation (48) shows the fraction ionised depends upon U, p and T. Table 6 shows the ionisation of Ca according to formula (48) at various T and p. It shows that calcium begins to get appreciably ionised at temperatures of about 4000°K, and ionisation is promoted by a reduction in pressure. But actually electrons arise from many other sources and therefore it is better to take its concentration as an independent constituent. The complete form of the equation is therefore

$$\ln \frac{n^+}{n} p_e = -\frac{U}{RT} + \frac{5}{2}\ln T + \ln \frac{(2\pi m_e)^{3/2} k^{5/2}}{h^3} + \ln \left\{ 2\frac{F_e(M^+)}{F_e(M)} \right\}. \quad (49)$$

The formula is also applicable to ionisation at any stage from M^r to M^{r+1} where M^r denotes the atom which has lost r-electrons, U_r the heat of ionisation from M^r to M^{r+1}, $F_e(M^r)$, $F_e(M^{r+1})$ the corresponding electronic partition functions. We have

$$\ln \frac{n_{r+1}}{n_r} p_e = -\frac{U_r}{RT} + \frac{5}{2}\ln T + \ln \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} + \ln \left\{ 2\frac{F_e(M^{r+1})}{F_e(M^r)} \right\}. \quad (50)$$

where $$F_e(M^r) = g_{r,o} + \Sigma' g_{rs} e^{-X_{rs}/kT},$$

$g_{r,o}$ being the weight of the ground-state of M^r, g_{rs} the weight of any excited state 's', X_{rs} the excitation-energy of the excited state s. If we express p_e in bars (dynes/cm²), the heat of ionisation in ionisation potentials and convert to natural logarithms, we obtain the equation

$$\log \frac{n_{r+1}}{n_r} p_e = - \chi_r \frac{5040}{T} + \frac{5}{2} \log T - 0{\cdot}48 + \log 2 \frac{F_e(M^{r+1})}{F_e(M^r)}. \quad (51)$$

From this formula, the value of n_{r+1}/n_r can be calculated for any atom, either neutral or r-times ionised, provided χ_r is known. $F_e(M^{r+1})$, $F_e(M^r)$ can be written out from the electronic structure but the actual values of χ_r, χ_{rs} and excitation potentials have to be obtained from spectroscopic data.

Formula (51) is of wide use in stellar physics, and Unsöld has described a nomographic method of calculating the values of n_{r+1}/n_r for any element, whose χ_r and other characteristics are known. See Unsöld, *Physik der Sternatmosphäre*, Chap. IV. pp. 66—87.

Applications :

Equation (48) and its more complete form (47), and other variations of (47) for non-equilibrium cases have been applied widely to diverse problems of Physics and Chemistry amongst which the following may be mentioned :—

(a) Astrophysics (Physics of the sun, the stars and nebulae). See Unsöld, *Physik der Sternatmosphäre* for a comprehensive account, or any book on astrophysics.

(b) Electrical conductivity of flames, (*Rev. Mod. Phys.* Vol. 3, p. 156).

(c) Formation of the electrical arc. (Engel and Steenbeck : *Elecktrische Gasentladungen*).

(d) Formation of the Ionosphere (Pannekoek, *Amst. Proc.* 1926; Saha and Rai, *Proc. Nat. Inst. Sci.*, **4**, 319).

This is a non-equilibrium case. The ionosphere is formed by the action of the sun's ultraviolet light on the gases of the earth's upper atmosphere. The amount of ionisation can be calculated if we have a knowledge of the intensity of solar radiation in the relevant ultraviolet parts, and knowledge of the spectroscopy of the atmospheric gases.

(e) Determination of the electron affinity of halogens.

A short account of these applications, and of the experimental proof of the correctness of formula (48), and of its multifarious applications will be given in the following sections.

18·17. Applications to the Fraunhofer, Spot and Flash (chromospheric) Spectra of the Sun.—As mentioned in §15·12 and §15·52—15·56, the lines of the Fraunhofer spectrum of the sun originate from the absorption by the gases of the solar atmosphere of the continuous light proceeding from the sun, excepting such lines like the A, B and a bands which arise from absorption in our own atmosphere (Telluric lines). Leaving aside these, the occurrence, intensity and other characteristics of the Fraunhofer lines yield us valuable information on the occurrence, abundance, and physical state of elements in the sun.

Since on cosmological theories, the earth is taken to have been formed out of a fragment of the sun detached from it by some cosmological process happening billions of years ago, the sun should be composed of the same elements as the Earth for which a detailed analysis has been made. According to these analyses there are 92 different elements in the earth's crust, with their abundance as given in Note 19. Do we find all these elements in the sun, and with the same abundance as on the earth?

We find that this is certainly not the case. Only 64 elements have been identified with the aid of their characteristic lines in the sun, and the abundance of the individual elements appears to be quite different.

We illustrate some of the problems raised by a close examination of Fraunhofer spectrum with the aid of the data on the lines of alkalies and alkaline earths, given in table 10. The second column shows the ionisation potentials of alkalies, the third and fourth the percentage of neutral atoms calculated according to the simpler formula (48) which as we shall see, holds almost rigorously for the alkalies; the sixth and seventh columns show the intensities of the absorption lines in the sun and the spot according to an arbitrary scale. Beginning with Na, we find that resonance lines are quite strong in the Fraunhofer spectrum, showing presence of considerable amounts of unionised Na in the normal atmosphere of the sun. But the corresponding lines of potassium are feeble and Rb and Cs are altogether absent. The absence of Rb and Cs from the sun's atmosphere is difficult to comprehend as their abundance on the earth, *Table* 10.—*Percentage of neutral atoms in sun and spot.*

Alkali Elements	I. P.	Percentage of neutral atoms		Line (λ in Å. U.)	Intensity		Alkaline Earth	I. P.	Percentage of neutral atoms		Line (λ in Å. U.)	Intensity	
		4000°	6000°		Sun	Spot			4000°	6000°		Sun	Spot
Li	5·37	90·3	15	6308	0	5	Be	9·5	100	96·9	..	..	..
Na	5·11	81·5	9·6	5896 5890	20 30	0 90	Mg	7·6	99·7	80·8	5184	30	30
K	4·32	30·9	2·2	7699 7665	5 6	12 15	Ca	6·1	97·4	53·8	4227	20	40
Rb	4·16	21·9	1·7	7948 7800	ab	0 1	Sr	5·67	95·1	14·0	4607	1	4
Cs	3·81	9·3	·9	8943 8521	ab	ab	Ba	5·18	70	11	5535	ab	ab

though much less than those of Na and K, is sufficient for showing the lines. The explanation is given by the ionisation theory. Column (3) shows the ionisation of alkalies calculated from (48), taking $p=10^{-4}$ Atm. It shows that as the ionisation potentials of these elements are increasingly lowered, they are almost completely ionised in the sun. The lines of Rb^+ and Cs^+ lie in the far ultraviolet, and therefore even if they are present in the Fraunhofer spectrum, they would escape detection on account of ozone absorption which cuts off all light below λ 2950.

It was predicted from such arguments that Rb and Cs may be found in the spot in the neutral state. The verification of this prediction by H. N. Russell who discovered the infra-red pair of Rb (resonance lines) in some spot spectra taken by Brackett in the Mount Wilson Observatory, constitutes one of the early triumphs of the ionisation theory. The intensities of the lines of neutral K and Rb are increased in the spot spectra as shown in Table 10, in accordance with the predictions of the ionisation theory. Cs continues to be totally ionised even in the spot. A number of other elements show similar behaviour. Li, like Rb, is extremely faint on the disc, but is strengthened in the spot; still since its I.P. is less than that of Na, its high ionisation is to be attributed to other causes. In (I.P.=5 volts) is found only in the spot. Most of the rare earths excepting Yb and Eu are represented by their spark lines only, both on the disc and in the spot.

The *Alkaline Earths*,—A better test of the ionisation theory is provided by the two-valence elements, because in these cases, the resonance lines of both the normal and ionised elements are within range. Taking for example Ca, the normal structure is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$, and the arc lines are produced by jumps from higher orbits. The resonance lines are given by $4s^2\ {}^1S_0$—$4s\ 4p\ {}^1P$, ${}^3P$, ${}^1S_0$—${}^1P_1$ being the line λ 4227, denoted by Fraunhofer as the *g*-line. The other line ${}^1S_0$— ${}^3P_1$ λ 6573, though it is the first to be excited is rather faint. The electron constitution of ionised calcium is like that of K $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s$, and the resonance lines are $4s\ {}^2S_{\frac{1}{2}}$ —$4p\ {}^2P_{\frac{1}{2},\ \frac{3}{2}}$. These lines are at λ 3968, 3933, and are represented by the great H and K-lines of Fraunhofer. The right hand side of Table 10 shows that the are lines are intensified in the spot, and observation also shows that the spark lines (due to ionised elements) are weakened. The same is true of Sr and Ba, but the latter appears to be completely ionised, for its resonance line is found neither on the disc nor in the spot, though it has the same I.P. as Na, viz., 5·1 volts, while Na-lines are very strong in both. This does not signify any violation of the ionisation formula but is due to the fact that the simple formula (48) no longer applies to these groups. We cannot neglect the last term $ln\ F$. Let us now use this and try to explain the discrepancy.

For Na, $F = 2F_e\,(\mathrm{Na}^+)/F_e\,(\mathrm{Na})$. Now since Na+ has the constitution $1s^2\ 2s^2\ 2p^6\ {}^1S_0$, $g_0=1$ and $F_e\,(\mathrm{Na}^+) = 1 + \Sigma g e^{-h\nu/kT} \doteq 1$, as $h\nu$ is very large. $F_e\,(\mathrm{Na}) = 2 + g e^{-h\nu/kT} \doteq 2$, neglecting the other terms. Hence $F = 1$, $ln\ F = 0$ and equation (48) applies to Na and the other alkalies.

This is not however the case with the alkaline earths. Let us illustrate by taking the case of Ba. Leaving aside the closed shell, the valency electrons form the outermost $6s^2$ shell, giving an ${}^1S_0$ term, and $g=1$. If we neglect the excited terms, we get $F = 2\ F_e(\mathrm{Ba}^+)/F_e(\mathrm{Ba})$ $=4$, so that the ionisation formula is now

$$ln\ \frac{n^+}{n}\ p_e = -\ \frac{U}{RT} + \frac{5}{2}\ ln\ T + ln\ \frac{(2\pi m_e)^{3/2} k^{5/2}}{h^3} + ln\ 4.$$

It is as if the heat of ionisation U is diminished by $RT\ ln\ 4$ *i.e.*, at the temperature of the sun, by nearly $1{\cdot}985 \times 6000 \times 2{\cdot}3 \times {\cdot}602 \cong 16{,}000$ cals corresponding to ·7 volts, i.e., the effective I.P. drops from

5·12 volts to 4·22 which is nearly the I.P. for Rb, and therefore Ba is completely ionised in the sun.

B. N. Srivastava[1] has studied the ionisation of Ba in the vacuum furnace, and has shown that both Ba^+ and Ba have got low lying metastable states which must be taken into account for calculating its thermal ionisation. For Ba, the metastable states are given by $6s\,5d$ giving ^1D, ^3D terms. Taking only these into account, and neglecting higher terms we have, putting $hc/k = x$,

$$F_e\,(\mathrm{Ba}) = 1 + 3e^{-9034x/T} + 5e^{-9215x/T} + 7e^{-9596x/T} + 5e^{-11395x/T}$$

$$= 2{\cdot}8966.$$

For Ba^+, we have a metastable $5d$-level, giving $^2D_{3/2}$, $^2D_{5/2}$ having weights of 4 and 6. We have therefore

$$F_e\,(\mathrm{Ba}+) = 2 + 4e^{-4874x/T} + 6e^{-5675x/T} = 4{\cdot}7538.$$

Hence $F = 2F_e(\mathrm{Ba}+)/F_e(\mathrm{Ba}) = 3{\cdot}3$, and the considerations given above are not much modified.

As in the case of the alkalies and alkaline earths, we can calculate the ionisation of all elements in the sun and the stars by applying (47), and using appropriate values of T and p_e. It should however be borne in mind that the absorption lines by which the elements are detected are produced by the whole atmosphere of the stellar body lying over its disc. There is a temperature and a pressure gradient in the atmosphere, and there is certainly wide departure from thermodynamical equilibrium except at the lowest layers. Formula (47) cannot be used for finding out ionisation, unless it is suitably modified. These matters have received extensive attention from astrophysicists since 1921 and those who are interested are referred to books and representative papers given at the end of this chapter.

Spectra of Sunspots.—It has been known since medieval times that spots appear periodically on the surface of the sun. They are dark compared to the general body of the sun, and photographs show a vortex structure. They are evidently regions of low temperature; in fact the ratio of the total intensity of the umbra (the central dark part) to that of the general body is found to be ·42. From this applying the Stefan-Boltzmann law, the temperature of the spot is calculated to be 4600°K.

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[1] *Proc. Roy. Soc. Lond.*, **175**, 26, 1940.

The lowering of the temperature causes also a general change in the nature of Fraunhofer absorption, as already stated. Generally the arc lines of elements are intensified, and the spark line diminish in intensity. All this is in accordance with the theory of temperature ionisation. Further, as A. Fowler showed, the bands which he identified as being due to MgH and TiO are all intensified in the spectrum of spots. This also can be explained with the aid of the general equations of chemical equilibria.

Detailed studies of the occurrence of molecules in the sun and the stars, and in the sunspot spectra have been made by Russell, *Astrophys. J.* **79**, 317-342, 1934; E. S. Richardson, *Astrophys. J.* **73**, 216, 1931; **77**, 195. These studies make extensive use of formula of chemical equilibrium. The hydride and oxide bands predominate owing to the great abundance of oxygen and hydrogen in stellar atmospheres.

The Flash Spectrum.—The important differences between the Fraunhofer spectrum and the flash spectrum referred to in §15·52 are:

(1) The Fraunhofer spectrum shows only 5 lines of Balmer series, while the Flash spectrum shows no less than 35, almost up to Balmer continuum under favourable conditions.

(2) The He-lines like the D_3, which are completely absent from the Fraunhofer spectrum, except under very special circumstances, are strongly present in the Flash spectrum. Further, unlike other neutral atoms (see next para), the intensity of neutral He-lines is feeble on the photosphere, increases in intensity with height reaching a maximum at 2500 km, and vanishing at about 7500 km. The lines of He^+ are strong in the lower heights.

(3) The lines of neutral elements are confined to lower layers of the chromosphere. They disappear from the higher layers, and the lines of the ionised element come out in great strength with increased height, e.g. the g-line due to Ca disappears, from a height of 5000 km, but the H, K-lines due to Ca^+ persist in great strength up to 14000 km. In fact the spectrum of the upper chromosphere is largely made up of enhanced lines, and is more like the reversal of the Fraunhofer spectrum of a star of higher temperature like α-Cygnus (A Class).

Some of these deviations can be explained from the ionisation theory. As formula (49) shows the number of ionised atoms

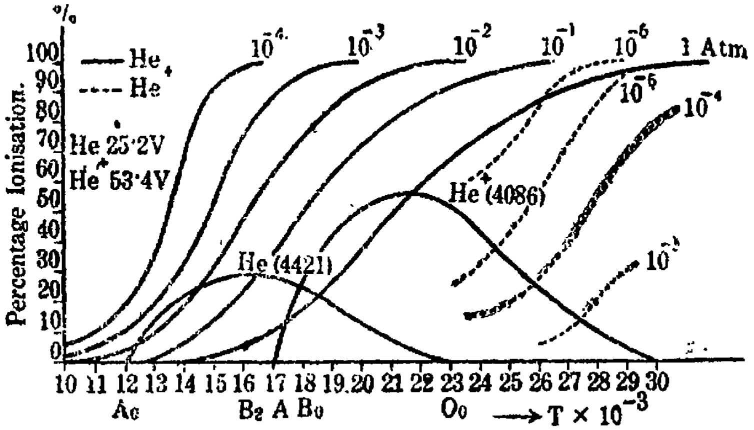

Fig. 7.—Increase of percentage ionisation with decrease of pressure.

depends not only on temperature, but also on electron pressure, i.e. on p_e. A reduction in electron pressure is always accompanied by an increase in percentage ionisation, as shown by Fig. 7 which is calculated for He.

The Fraunhofer spectrum of the sun, on account of the way in which it is obtained, comes from the lower layers, i.e. it is produced by a layer about 300 km. thick above the photospheric level. Here on account of high pressure the atoms are mostly neutral, except those with the lowest I.P. In the higher chromosphere, pressure is less, hence according to (49) almost all atoms get fully ionised.

Experiments also prove that the reduction of pressure causes an increase in ionisation. An arc run in vacuum always shows more lines of ionised atoms than of normal atoms. This is

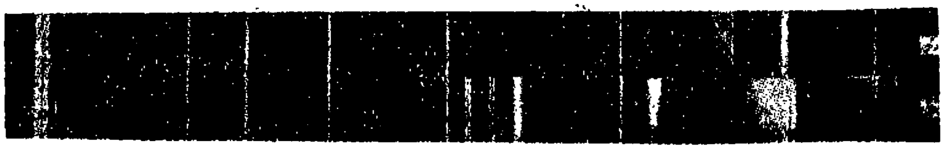

Fig. 8.—Development of the lines of ionised Mg in the vacuum arc.

illustrated by Fig. 8, reproduced from an early experiment by Fowler and Payne, of the spectrum of Mg-arc in the open and in vacuum. The open arc contains only lines of neutral elements and compounds, but in the vacuum arc, the line 4481 which is due to Mg^+ is developed.

From the foregoing sketch, it will be seen that the ionisation theory is very helpful in giving a general explanation of the Fraunhofer spectrum of the sun, and of its other features, viz. of the spots and faculae, and as we shall see later, of the spectra of stars as a whole, but there are many details which are outside the scope of this theory. For these modern books on Astrophysics like Unsöld's *Physik der Sternatmosphäre* or Rosseland's *Theoretical Astrophysics* may be consulted.

Attention may be drawn to some outstanding anomalies. It is almost certain that the Earth (and also the other planets) separated from the sun some billions of years ago, and started on independent careers of their own. The chemical composition of the earth and the sun should therefore be the same. This is not borne out by the data so far obtained on the chemical composition of the Earth's crust and the Sun's atmosphere, as particularly detailed in Note 19. Attention may be drawn here to one particular feature. The light elements Li and Be show wide divergence in abundance, it being about 1000 times larger in the Earth's crust than in the Sun's atmosphere though for other elements with similar chemical properties, the divergence in abundance is not so pronounced. It is assumed that at the temperatures prevailing inside the sun (the temperatures run to millions of degrees), reactions take place between high energy protons and nuclei of light elements (*Thermonuclear Reactions*) leading to the production of He, and consequently the Li and Be nuclei are consumed.

18·18. Application of the Ionisation Formulae towards a Physical Explanation of the Spectra of Stars.—

From the application of the laws of radiation as explained on p. 700 it has been found that the surface temperatures of stars vary from 3000°K for red stars to over 20000°K for white stars. The surfaces of stars therefore present the best material for the application of the ionisation formulae. The interiors of stars are at much higher temperature and the ionisation formula has been applied there too, but we have no means of verifying our conclusions there.

A systematic investigation of the spectra of stars was undertaken by the astronomer Sir Norman Lockyer between 1870 and 1900. He discovered the remarkable fact that inspite of their large numbers, the spectra of most stars can be classified into about five or six well defined groups, which show signs of a continuous transition from one stage to the other. The work was then continued at the Harvard College Observatory by Prof. Pickering and Miss Cannon. The result was in the main a confirmation of Lockyer's result, and can be described in the following words of Prof. H. N. Russell :—

> "The spectra of the stars show remarkably few radical differences in type. More than 99 per cent of them fall into one or the other of the six great groups which during the classic work of the Harvard College Observatory were recognised as of fundamental importance, and received as designations, by the process of the survival of the fittest, the rather arbitrary letters, B, A, G, F, K, M. That there should be so few types is noteworthy, but much more remarkable is the fact that they form a continuous series. Every degree of gradation between the typical spectra denoted by B and A may be found in different stars and the same is true to the end of the series, a fact recognised in the familiar decimal classification in which BA, for example, denotes a spectrum half way between the typical examples B and A. The series is not merely continuous, it is linear. There exists slight difference between the spectra of different stars of the same spectral class, such as A, but these relate to minor details. Almost all the stars of the small outstanding minority fall into three other classes (or rather four), denoted by the letters P, O, N, R. Of these, O undoubtedly precedes B at the head of the series, while R and N which grade one into the other come probably at its end, though in this case the transition stages are not clearly worked out"

General Features of Variation.—A general idea of the variation of stellar spectra can be gathered from Fig. 9 (p. 821) which is a modification of one originally due to Lockyer, and subsequently modified by Milne, and the analysis of the result is summed up in Table 11.

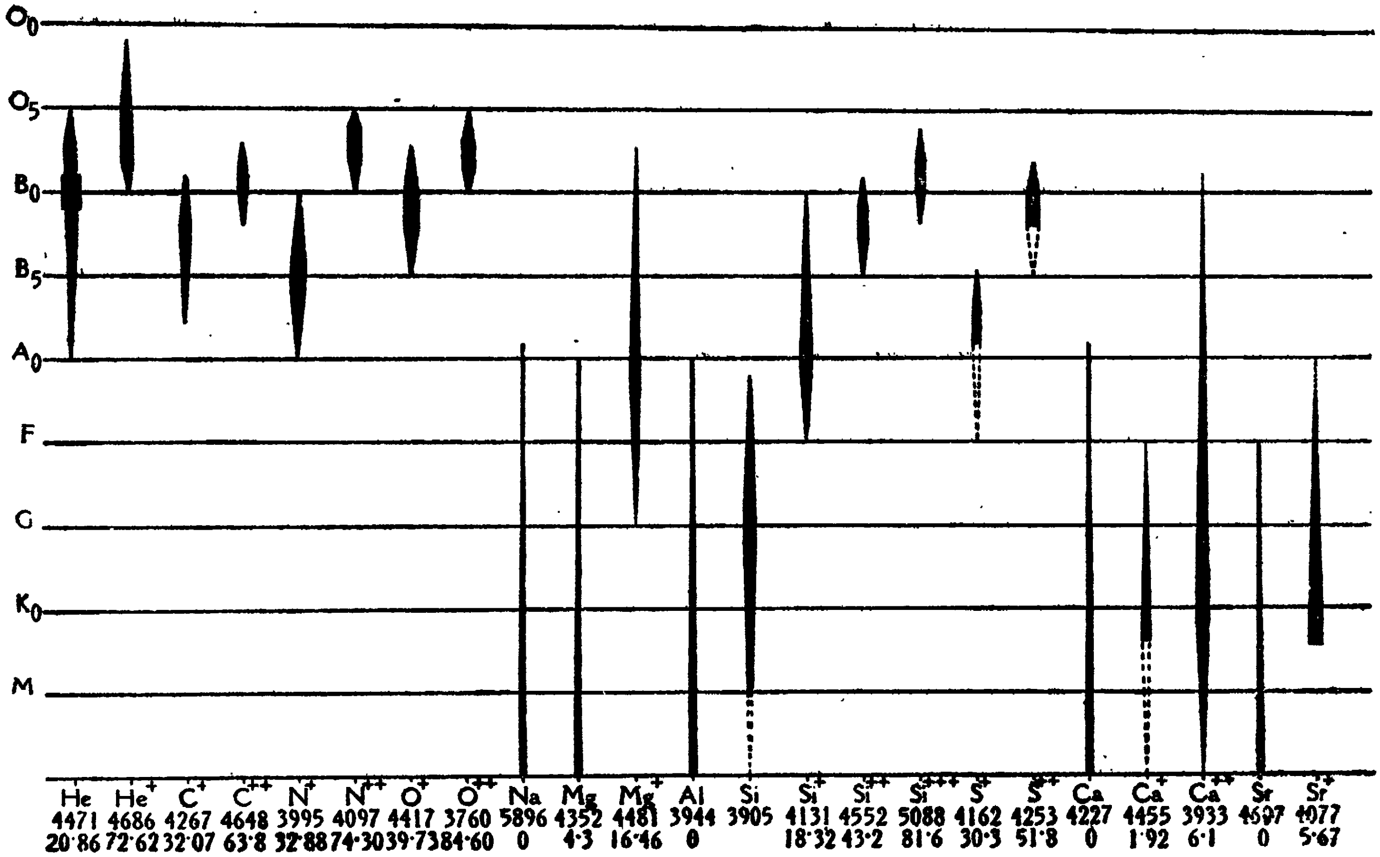

Fig. 9.—Lockyer's diagram illustrating variation of intensity of spectral lines in stellar sequence. The first row gives the name of the element, the second the wavelength of the characteristic lines, the third gives the excitation potential.

Table 11.—*Stellar Lines of Astrophysical Importance.*[1]

Element	Line λ in Å.U.	Spectral Description	Excitation Potential	Appearance	Maximum	Disappearance
H	4861 (Balmer series)	$2p-4d$ $-4s$	10·16		A_0	
He	4471	$1s\,2p-1s\,4d$ $^3P-^3D$	20·85	A_0	B_0	O_5
He^+	4686	$3d-4f$	72·62	B_0	O_7	O_1
C	..	..	..	..	..	..
C^+	4267	$2s^2\,3d-2s^2\,4f$ $^2D-^2F$	32·07	B_8	$B_{2,3}$	O_9
C^{++}	4648, etc. (Triplet)	$2s\,3s-2s\,3p$ $^3S-^3P$	63·8	B_2	$O_{8,9}$	O_7
N	..	..	..	..	..	..
N^+	3995	$2p\,3s-2p\,3p$ $^1P-^1D$	32·88	A_0	B_5	B_0
N^{++}	4097	$2s^2\,3s-2s^2\,3p$ $^2S-^2P$	74·30	B_0	O_7	O_5
O	..	..	..	..	..	..
O^+	4417	$2p^2\,3s-2p^2\,3p$ $^2P-^2D$	39·73	B_5	B_1	O_7
O^{++}	3760	$2p\,3s-2p\,3p$ $^3P-^3D$	84·64	B_0	O_9	O_6
Na	5896	$3s-3p$ $^2S-^2P$	0	Lowest	Lowest	B_9
Mg	4352	$3s\,4p-3s\,4d$ $^1P-^1D$	4·3	Lowest	$K_{2,5}$	A_0
Mg^+	4481	$3d-3f$ $^2D-^2F$	16·46	G_0	A_2	O_7
Al	3944	$3p-4s$ $^2P-^2S$	0	Lowest	Lowest	A_0
Al^+	3900·7	$3s\,4p-3s\,4d$ $^1P-^1D$	13·35			

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[1] For a fuller list, see Russell, *Astro. Journ.*, **61**, 223, 1925.

Table II.—(continued)

Element	Line λ in Å.U.	Spectral Description	Excitation Potential	Appearance	Maximum	Disappearance
Si	3905	$3p^2 - 3p\,4s$ $^1S_0 - {}^1P$	1·90	Lowest	G_0	A_2
Si^+	4131	$3d - 4f$ $^2D - {}^2F$	18·32	F_0	A_0	B_3
Si^{++}	4552	$3s\,4s - 3s\,4p$ $^3S - {}^3P$	43·2	B_5	B_2	O_0
Si^{+++}	4088	$4s - 4p$	81·6	B_2	O_4	O_6
P						
P^+						
S						
S^+	4162	$3p^2\,4p - 3p^2\,4d$ $^4D - {}^4F$	30·3		B_8	
S^{++}	4253	$3p\,4s - 3p^2\,4p$ $^3P - {}^1D$	51·8		B_1	O_8
Ca	4227	$4s^2 - 4s\,4p$ $^1S_0 - {}^1P$	0	Lowest	Lowest	B_9
	4455	$4s\,4p - 4s\,4d$ $^3P - {}^3D$	1·92		K_2	F_0
Ca^+	3933(K) 3968(H)	$4s - 4p$ $^2S - {}^2P$	6·1	Lowest	K_0	O_9
Sr	4607	$5s^2 - 5s\,5p$ $^1S_0 - {}^2P$	0	Lowest	Lowest	F_8
Sr^+	4077 4215	$5s - 5p$ $^2S - {}^2P$	5·67		K_2	A_0
Ba	5535		6			
Ba^+	4904 4554	$6s - 6p$ $^2S - {}^2P$	5·18		M	A_3

Explanation of the table :—

The first column contains the name of the elements, the second column the particular characteristic line by which it is detected. The third column gives the spectral designation of the line in the standard spectroscopic notation (Russell, Saunders and Shenstone), column 4 gives the excitation energy in electron volts for raising the neutral atom from the normal state to the particular state in which it can absorb the line. Thus for the Si^{++} line λ 4552, etc., the excitation voltage is calculated as follows. We start with normal Si. The first I. P. is 8·12 volts, the second I. P. is 16·26 volts. The normal state of Si^{++} is $1s^2\ 2s^2\ 2p^6\ 3s^2$. But in this state Si^{++} can absorb the line $3s^2.\,{}^1S_0 \rightarrow 3s\ 3p.\,{}^1P_1$ which is in the Schumann region.

The particular group of astrophysical lines λ 4552, etc. is due to the transition $3s\ 4s \leftarrow 3s\ 4p$. Hence we must add an amount of energy which can raise the electron in Si^{++} from the $3s^2$-stage to the $3s\ 4s$ stage. According to A. Fowler, this energy is equivalent to 18·9 volts. Hence the excitation potential of the line is $8{\cdot}12+16{\cdot}26+18{\cdot}9 = 43{\cdot}3$ volts. Lines like λ 4227, which are the resonance lines of normal atoms, require no preliminary excitation. Their I. P. is put equal to zero.

In the fifth column, the particular stellar class at which a line just appears is given. The principal lines of normal atoms appear in stars with the lowest temperature, but the subordinate lines or enhanced lines appear only at a certain higher stage depending upon the excitation required. The temperature of this stage is generally higher, the higher the excitation potential, e.g., compare He λ 4471 for which the I. P. is 20·86 volts, and which appears at a stellar surface having the temperature 10000°K.

In the sixth column the stage at which the intensity of the line is maximum is given. The maximum is generally flat. The maximum enables us to calculate the electron pressure as first pointed out by Fowler and Milne (vide §18·19.)

The seventh column gives us the stage at which the line disappears. If it is a principal line like the Ca g-line, the disappearance means that the element is about 99% ionised. If the line belongs to a subordinate series, the percentage ionisation may not be so complete. The temperatures under each class, and the electron pressures are calculated from the application of the ionisation theory.

The table as well as Fig. 9 shows that the lines of an element just appear at a certain stage, rise to a maximum and disappear at the other end. Thus the helium line λ 4471 just appears at the

A$_0$-class, rises to a maximum intensity at the B$_0$-class (indicated by maximum thickness of the line representing He λ 4471 in Fig. 9) and disappears at the O$_5$-class. Or take particularly the case of silicon. We find that it is present in three successive stages of ionisation which succeed and partly overlap each other in the stellar range.

The explanation of these facts is at once suggested by the ionisation theory. Thus the disappearance of the silicon line λ 3905 at A$_2$ denotes that Si is completely ionised at this temperature. The appearance of the Si$^+$ line λ 4131 at the F-stage indicates that silicon is considerably ionised at this stage, and further excited to the level $3d$ in which it can absorb the line λ 4131.

For the sake of numerical illustration, we take the g-line of Ca. This has maximum intensity in stars with the lowest temperature and disappears at A$_0$. The presence of maximum at the lowest temperature is easily understood, for the g-line is a principal line and can be absorbed by Ca-atoms in their normal state. The concentration of normal calcium atoms is maximum at the lowest temperature, since at higher temperatures, their proportion is diminished by excitation to higher levels and by ionisation. The disappearance at the B-stage is due to complete ionisation of calcium. A glance at Table 9 shows that if we calculate according to the simple ionisation formula, the ionisation of calcium becomes complete at $T=13000$°K, $p=1$ atmos, or at $T=9000$, $p=10^{-3}$ atmos. We cannot find out the exact temperature of the A-class unless we make some assumption regarding the value of the pressure on stellar atmospheres. In the early investigation pressure was assumed to vary from 1 atmos. to 10 atmos. In this way, the following results were compiled.—

Appearance of K	(3933)	M	Ionisation of Ca begins at 4000°K
Disappearance of g	(4227)	B	Ca completely ionised at 13000.
Appearance of Mg$^+$	(4481)	G	Mg considerably ionised at 7000.
Disappearance of K	(3933)	O	Ca$^+$ completely ionised at 20000.
Disappearance of Mg$^+$	(4481)	O	Mg$^+$ completely ionised at 23000.

The method is however uncertain owing to a number of reasons. First of all, the pressure is chosen arbitrarily. Secondly only a qualitative account is taken of the fact that the different lines require different amounts of material for their production. A well-known example is that of sodium D-line. It is found that the smallest amount of sodium (10^{-7} gm/cm^3) in a flame will bring out the principal lines very strongly, while much larger amounts are required to bring out the subordinate lines in the same region. Thus the formula cannot be applied for any quantitative purpose unless the amount of matter required for the marginal appearance of a line is known.

18·19. Electron Pressure from Maximum Intensity of Subordinate Series Lines and Enhanced Lines (Fowler and Milne).—A very elegant method for determining the electron pressure was discovered by Fowler and Milne. They observed that there is a remarkable difference in the variation of intensity of the principal lines of neutral elements and of their subordinate lines in the stellar sequence. The principal lines of neutral elements are most intense at the lowest temperatures and gradually die out with increase of temperature (vide the behaviour of Ca g in Fig. 9). But the subordinate line or lines of an ionised element appear at a stage depending on its excitation potential: they

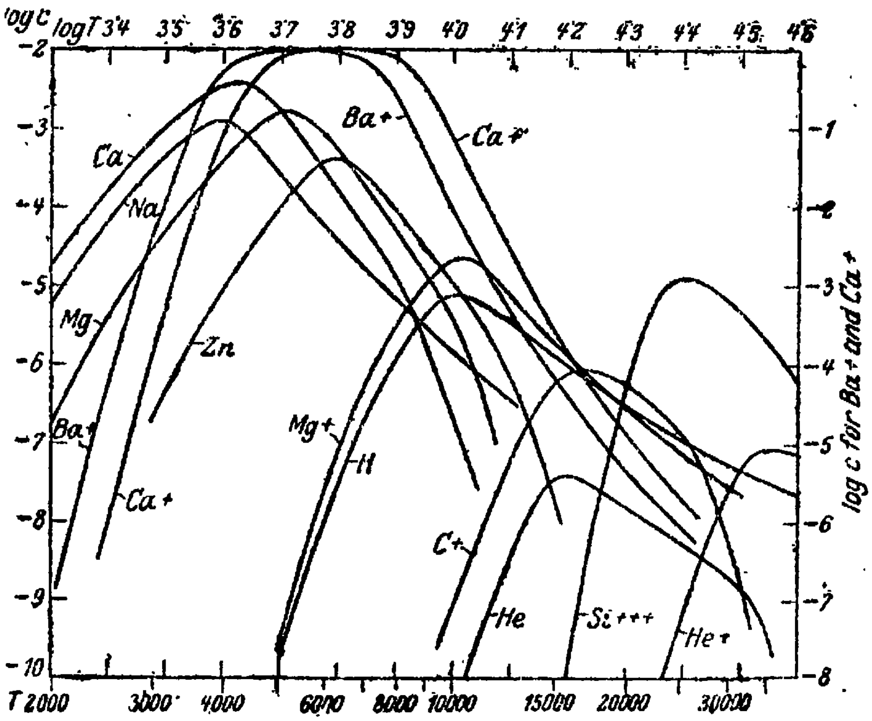


Fig. 10.—Variation of intensity of lines of subordinate series and enhanced lines of elements with temperature. The abscissae represent temperatures, the ordinate concentrations of excited atoms.

are at first very faint, gradually rise to a maximum at some intermediate stage and then again fall off to zero intensity as shown in Fig. 10.

Fowler and Milne explain the phenomenon in the following way :—At the lowest temperature all atoms are in the normal state, there are none in the higher states. With increase of temperature, the higher states begin to come out. When the temperature still further rises, the atoms begin to get ionised, and the proportion of atoms in the excited states begins to fall off. A maximum must have been reached in the interval.

When the above ideas are translated into mathematical language, and conditions for maximum concentration of excited levels applied, we get a relation connecting the electron pressure in the reversing layer, and the temperature at which maximum intensity is reached. From eqn. (49) we have, denoting the fraction of ionised atoms by x,

$$\frac{x}{1-x}\,p_e = e^{-\chi_1/kT}\,T^{5/2}\,2I\,\frac{F_e(\mathrm{M}^+)}{F_e(\mathrm{M})}\,. \qquad (52)$$

Applying the condition for maximum of the line whose resonance potential is $\chi_1-\chi_r$, we get

$$p_e = \frac{\chi_r+\frac{5}{2}kT}{\chi_1-\chi_r}\,.\,e^{-\chi_1/kT}\,T^{5/2}\,2I.\,\frac{F_e(\mathrm{M}^+)}{F_e(\mathrm{M})}\,; \qquad \frac{x}{1-x}=\frac{\chi_1-\chi_r}{\chi_r+\frac{5}{2}kT}\,. \qquad (53)$$

where χ_1 is the ionisation potential.

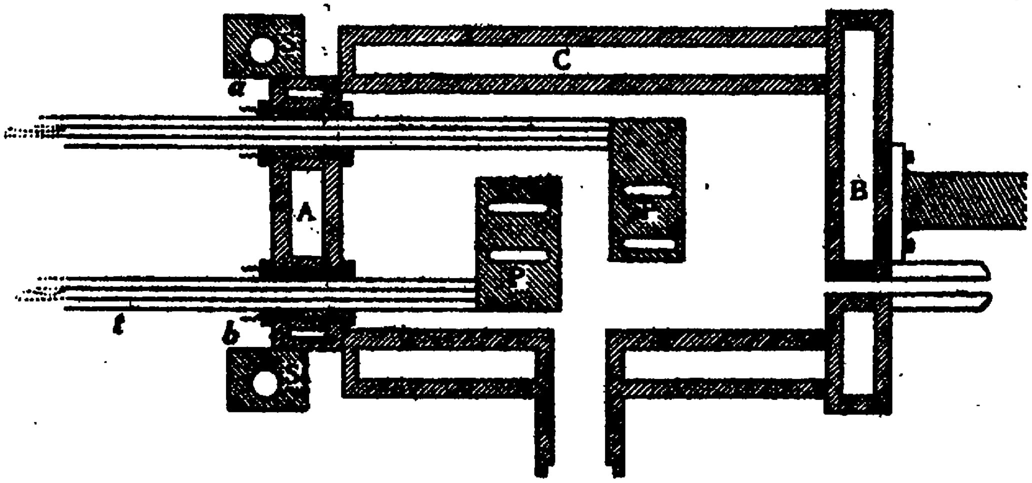
As an example of the application of Fowler and Milne's formula, we take the case of the zinc triplet ^{3}P—^{3}S, λ 4810, 4722, 4680 (vide Fig. 10). They attain the maximum intensity at the G_0-stage where the temperature may be supposed to lie between 5000° and 7000°; we have in this case $V_0=9\cdot34$ volts, $V_r=5\cdot33$ volts, $F_e(\mathrm{Zn}^+)=2$, $F_e(\mathrm{Zn})=1$. Substituting proper values in (53) we obtain

for $T=$ 5000°, $p_e=1\cdot38\times10^{-6}$ atmos, $x=\cdot61$
6000° $=8\cdot0\times10^{-5}$,, $=\cdot62$
7000° $=1\cdot6\times10^{-3}$,, $=\cdot63$

where x is the fraction ionised.

These pressures are very much smaller than the pressure of one to 10^{-2} atmospheres formerly chosen. To obtain consistent values of T and p_e for stars of different types, all available data should be discussed and sifted. This has been done by Fowler and Milne, by Cecelia H. Payne and Pannekoek, and the reader may be referred to the original papers. The final results do not appear to be concordant.

18·20. Experimental Proof of the Theory of Thermal Ionisation.—The direct experimental proof of thermal ionisation has been secured by a large number of workers, Saha, Srivastava, Tandon and other workers in the University of Allahabad, Mayer, Langmuir, and King. The first mentioned workers used for the purpose a demountable furnace of the type shown in Fig. 11, which is a modification of the vacuum graphite furnace first extensively used by R. W. King in the Mount Wilson Observatory for study of excitation of spectra of elements by heat. For details the original paper may be consulted.



F.g. 11.—Vacuum graphite furnace used for thermal ionisation experiments.

The final form of the high temperature vacuum furnace which has been used at Allahabad for experiments on thermal ionisation and for determining the electron affinity of elements is shown in figure 11. A and B are hollow cylindrical cast-iron plates and C is a hollow cylindrical cast-iron drum. These can be all water-cooled. Their vertical faces are all ground plane. C is mounted on wheels on a lathe bed, A is fixed vertically at one extremity of the lathe bed by the support S S, and B is carried on the axle of a shaft which can be moved by means of a differential screw. When all internal arrangements are complete, the system can be sealed by moving the drum C and the plate B.

A carries the water-cooled, insulated leads 'a' and 'b' to the copper collars P and P, which hold the Acheson graphite tube F (see Fig. 12). High amperage current passes through 'a' to the block P, through the graphite tube F, to P, b and back to the low-tension transformer. A contains two other holes c and d, of which one is for carrying electrical connections. The evacuation takes place through the tubes attached to c and d by means of powerful mechanical and diffusion pumps.

The other fittings are shown in Fig. 12. A is the subsidiary graphite furnace which was heated by conduction of heat. Temperature at the bottom of this furnace where the substance to be vaporised is kept, can be measured by means of a calibrated thermocouple placed there.

When a substance like NaCl is to be studied, it is placed in the furnace A. It gets vaporised, and the vapour is dissociated into Na^+ and Cl^- within F. The products of dissociation effuse out through a narrow hole in the graphite tube and either the positive or the negative currents due to Na^+ and Cl^- respectively, can be made to pass to the Faraday cylinder E by means of accelerating and retarding potentials and the ionic currents measured by a sensitive galvanometer. Thus the reaction $NaCl \rightleftarrows Na^+ + Cl^-$ can be studied at different temperatures and pressures. Free electrons are deflected away by means of a magnetic field produced by the coils MM. From the values of the current, the value of the reaction constant characteristic of the dissociation can be calculated.

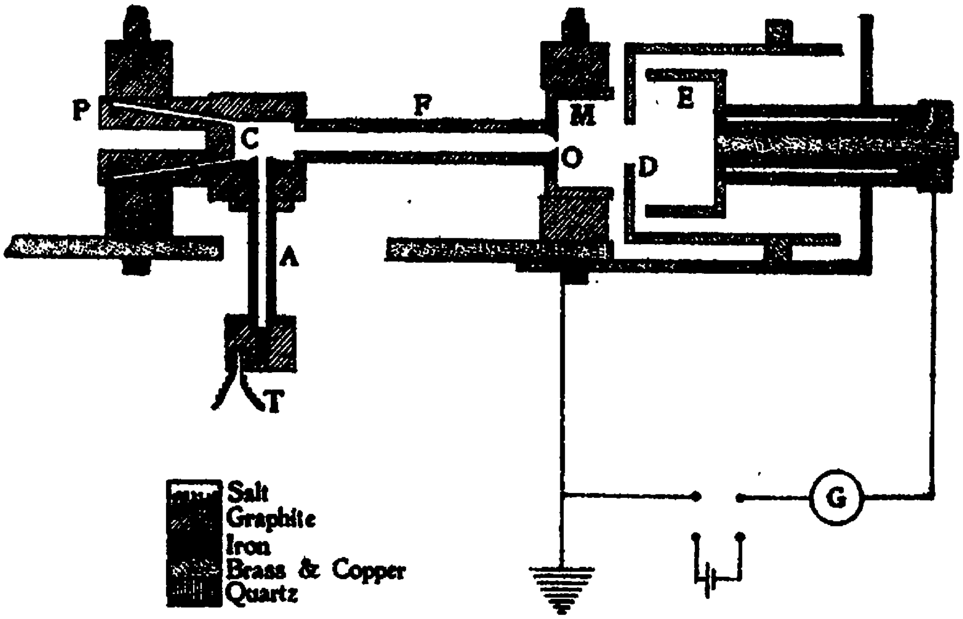


Fig. 12.—Scheme of arrangement inside the vacuum furnace.

Much earlier than the formulation of the ionisation theory King showed by heating elements in his vacuum furnace that they can be brought to luminescence by heat alone, and lines which have low excitation potential come out first and others in the increasing order of their excitation come later. We illustrate this by a simple example.

Let us take the Ca-atom. The structure is $1s^2.2s^2.2p^6$ $3s^2.3p^6.4s^2$. The normal state is $4s^2$ $^1S_0$; the higher states are $4s\,3d.$ ^1D, ^3D; $4s\,4p.$ ^1P, ^3P. The line $^1S_0-{}^3P_1$, $\lambda=6573$, has the lowest excitation potential $\chi_{r,s}=1\cdot88$ volts and comes out first at the lowest temperature. Then comes out the line $^1S_0-{}^1P$, $\lambda=4227$ which is known as the g-line. When the temperature is still further increased the other lines come out. At about 2000°K, the H, K lines $\lambda=3968$, 3933, which are the resonance lines $4s$ $^2S_{\frac{1}{2}}-4p$ $^2P_{\frac{1}{2},\frac{3}{2}}$, of Ca$^+$ begin to come out, at first feebly, then very strongly. The same succession of appearance of lines was observed by early spectroscopic workers like Lockyer and Fowler in the spectra of the flame, the arc and the spark. The flame shows the 'g' line strongly, and the H, K very feebly, if at all. In the arc the H and K are strengthened, in the spark spectrum H and K are very strong and 'g' is almost vanishing. They represent gradually increasing temperatures viz. flame $\simeq$ 2000°K, arc 3500–4000°K, spark 6000°K.

Very convincing proof of the correctness of the ionisation theory was obtained by King and Russell by first heating Ca to a high temperature, so that the H and K lines came out strongly in emission; then a little Cs was added. This had the effect of almost completely quenching the H and K lines.

The explanation is very simple. We can write out (49) in the form

$$n_e n_+/n_a = \frac{(2\pi mk)^{3/2}}{h^3}\, T^{3/2}\, e^{-\chi/kT}\, g_e\, g_i/g_a. \qquad (54)$$

At 2000°K, putting proper values, we can easily see that $n_e n_+/n_a$ $=5\cdot5\times10^5$ for Ca, and $4\cdot8\times10^{10}$ for Cs. Now at first, we had only Ca. Supposing the pressure rose to be 1 atm. we have $n=p/kT$ $=3\cdot7\times10^{18}$ per c.c. Then from $n_e n_+/n_a=nx^2$, taking x to be small we get $x=4\times10^{-7}$ and $n_e=n_+=1\cdot5\times10^{12}$/c.c. When we put Cs, we find by a similar calculation $n_e=4\cdot2\times10^{14}$ i.e. the number of electrons is nearly 300 times increased. The effect of this on Ca-ionisation is to reduce Ca$^+$ nearly 300 times, as the product $n_e n_i$ must remain constant. So the H and K-lines are quenched.

In the experiments of Saha, Sur, and other co-workers the electrical conductivity of the heated vapour was measured with very low e.m.f. between the electrodes. No appreciable conductivity was found with vapours of Zn, Cd, Hg which have I.P's varying from 9 to 10·5 volts even at temperatures of 2000°K. Mg (I. P.=7·61 volts) also gave no evidence of being ionised. But with the alkali metals the ionisation was so great at 2000°K, that currents of the order of milliampere were reached.

These experiments were qualitative, but quantitative experiments[1] on the thermal ionisation of Ba and Sr, were carried out by B. N. Srivastava and of Li, Na, K, Ca, Al by B. N. Srivastava and A. S. Bhatnagar. These experiments completely established the correctness of formula (47).

The Electron Affinity of Halogens.

The valency electrons of halogens form p^5-shells, and it requires only another electron to make the shell complete like that of inert gases. The halogens have thus an affinity for electrons which can be expressed by the symbol

$$\mathrm{Cl}+\mathrm{e}=\mathrm{Cl}^-+A. \qquad (55)$$

'A' is a positive quantity and may be expressed in volts, and called the "Electron Affinity Potential." It is not possible to obtain it spectroscopically, as the capture spectrum is not known. Various methods have been given for calculating them theoretically and determining them experimentally. The results are shown in Table 12, p. 832.

The best method[2] of finding out these quantities is from an experimental study of the dissociation of alkali halides in the vacuum furnace. When we heat an alkali halide say NaCl in the vacuum chamber, the following reactions take place:—

$$\begin{aligned}\mathrm{NaCl} &= \mathrm{Na}+\mathrm{Cl}-D\\ \mathrm{NaCl} &= \mathrm{Na}^+ +\mathrm{Cl}^- -Q\\ \mathrm{Na} &= \mathrm{Na}^+ +\mathrm{e}-U\\ \mathrm{Cl}+\mathrm{e} &= \mathrm{Cl}^- +A.\end{aligned}$$

It is easy to see that from the first law of thermodynamics we have

$$A=D+U-Q. \qquad (56)$$

---

[1] *Proc. Roy. Soc. Lond.*, **176**, 343, 1940; *Proc. Nat. Acad. Sci. India*, **15**, 1946 and other papers.

[2] See for a complete account, Experimental Determination of the Electron Affinity of Chlorine by M. N. Saha and A. N. Tandon, *Proc. Nat. Inst. Sci*, **3**, 287, 1937; A. N. Tandon, *Ind. Jour. Phys.* **11**, 99, 1937; B. N. Srivastava, *Proc. Nat. Inst. Sci.* **5**, 313, 1939.

Of these quantities, D is obtained from chemical data, from the heat of formation of NaCl out of sodium and chlorine; U the I. P. of sodium is well-known. We have only to determine Q, the heat of formation of NaCl out of Na^+ and Cl^-.

In these experiments, as explained earlier, a small quantity of NaCl is vaporised at a definite pressure in the subsidiary furnace, and the vapour of NaCl is dissociated into Na^+ and Cl^- in the main furnace. The concentrations of Na^+ and Cl^- are obtained by measuring positive and negative effusion currents. From the value of these currents, we can determine the Reaction-isobat K over a range of temperatures and pressures. We obtain Q from the law of reaction isobar:

$$\log K = \log \frac{p_{Na^+} \cdot p_{Cl^-}}{p_{NaCl}} = -\frac{Q}{2 \cdot 3RT} + \frac{5}{2} \log T + \log \frac{8\pi^2 IkT}{h^2}$$
$$+ \log \left(1 - e^{-h\nu/kT}\right) + \log \left[\frac{(2\pi)^{3/2} k^{5/2}}{h^3} \left(\frac{m_{Na^+} \cdot m_{Cl^-}}{m_{NaCl}} \right)^{3/2} \right] \quad (57)$$

Table 12.—Electron Affinity of Electronegative Elements.

Value Element	Allahabad School (in K. cal.)	Mayer & others (in K. Cal).	Value in e. v.
F			7·1
Cl	86·6 Saha & Tandon	86·5 (Helmholtz)	3·70
Br	79·5 Srivastava	80·5 (Doty)	3·45
I	74·5 Srivastava	72·4 Sutton	3·23
H			0·749
O		70·8 (Vier)	3·07

For electron-affinity of H, See Hendrich, *Ap. J.* **99**, 59; for that of O, Vier and Mayer, *J. Chem. Phys.* **12**, 28, 1944. The value of 7·1 for F is an extrapolated one and still needs experimental confirmation.

Like the halogens, H has also electron-affinity which has been calculated from theoretical considerations to be ·747 volts. The H^- ion has been shown by Wildt and Chandrasekhar and their coworkers to exist in great strength in the sun and the star, and is responsible for the largest part of the opacity of the solar and stellar atmospheres, by the bound-free (absorption of solar radiation by H^- causing ejection of electrons) and free-free (deflection on account of light absorption of electrons approaching H^- to other hyperbolic orbits) transitions of the electron in the field of the H^- atom.

Other electronegative elements like O and S possess electron-affinity like halogens; of these that of O has been calculated to be 3·07 volts. This should be capable of experimental verification. The O^- ion plays some part in causing opacity of the atmospheres of cooler stars.

18·21. Thermonuclear Reactions.—As we have seen in §18·18 the atmospheres of cool stars contain only neutral atoms and molecules. With the rise of temperature, ionised atoms begin to appear, stage by stage, but there is hardly any atom which loses more than 3 or 4 outermost electrons even in the hottest class of stars (O-class). Silicon $1s^2\,2s^2\,2p^6\,3s^2\,3p^2$ is a good example. We have again to remember that there is a big gap in the ionisation potentials of electrons in the outermost shells and of electrons in the first closed shell, e. g. Na, and Na^+ and Mg and Mg^{++}. The I. P. of Na is only 5·12 volts, that of Na^+ is nearly 47 volts. The important lines of ionised elements like Na^+ are usually in the extreme ultra-violet and therefore even if such elements exist we cannot observe them. In Nova or new stars which are due to some kind of explosion which blows off a part of the outer mantle and in Wolf-Rayet stars which are probably remnants of old Nova, and in some other peculiar stars, we sometimes obtain atoms with a high degree of ionisation. If we compare giant stars with dwarfs of the same temperature class, the giants are found to show higher grade of ionisation in accordance with equation (51), because the atmosphere of giants is very much extended and pressure is extremely low.

The highest stellar temperature scarcely exceeds 50,000°C in O-type and about 10^5 in Wolf-Rayets. According to the theories of stellar structure initiated by Sir A. Eddington, the temperature increases rapidly towards the interior. According to Blanch and others the central temperature of the sun is given as 26×10^6 (26 million degrees). The pressure is also very high viz. $9\cdot7\times10^{10}$ gm. per cm^2, i.e. $8\cdot47\times10^8$ times the Earth's atmospheric pressure, and the central density reaches the value 110 gm/cm.^{3}

It is obvious that in the interior of stars, the lighter elements which form the major components of the star will be completely ionised. Calculation shows that even a comparatively heavy element like Fe loses its last electron. The ionisation potential of the last electron in Fe is about 9600 volts. Applying (51) we find that

$$\log n^{26}/n^{25} = -\frac{5040}{T}\chi + \tfrac{5}{2}\log T - 6\cdot 5 - \log p_e$$

where p_e is expressed in atmospheres. Putting $\chi = 9{,}600$ volts, $T \cong 10^7$ °C we find $\log (n^{26}/n^{25}) = -1\cdot 8$, if $p_e \cong 10^8$ atmospheres, i.e. a considerable proportion of Fe is completely stripped of all electrons.

As lighter atoms form 99% of the constituents of the star, we may assume, though the argument cannot be supported by experimental evidence, that the interior mainly consists of bare nuclei and electrons. The mean molecular weight $\overline{M}$ will depend on the relative abundance of elements. If the star consists almost wholly of H, $\overline{M} = \frac{1}{2}$; for He, $\overline{M} = 1\cdot 33$ and for heavy elements $\overline{M} > 2\cdot 2$. Hence any value of $\overline{M}$ between $\cdot 5$ and 2 is possible, according to the composition of the star.

Energies Evolved in Thermo-nuclear Reactions.

If the stellar matter in the interior of star consists mostly of bare nuclei, densely packed, and of free electrons, it is known from nuclear physics that the nuclei on account of their motion would act upon each other and produce nuclear reactions. For example if we take a temperature of $2\cdot 6 \times 10^7$ we have the mean kinetic energy of the molecules $\cong 4 \times 10^9$ ergs which is equal to 2,500 electron-volts. This energy is too small for starting any nuclear reaction, but on account of Maxwellian distribution a fraction of protons and neutrons will possess kinetic energies of the order of 10^4 e.v. or more, at which many nuclear reactions start between protons, deuterons and other light particles as shown in Table 13.

Explanation of the Table.—Column (1) gives some of the nuclear reactions of the proton, neutron and the deuteron, and also reactions of these with heavier nuclei. The left side in column (1) gives us the participants, the right side the products of reaction; the symbol $Li^7 + H^1 \rightleftarrows 2He^4$ denotes that a lithium nucleus of weight 7 when bombarded by a proton gives us ultimately two helium nuclei. Experiments have shown that though many other intermediate reactions are possible, the ultimate products are two helium nuclei. Though the reaction is exothermic, experiments have shown that the proton must possess a minimum velocity before the reaction can start. This quantity is

Table 13.—*Energies evolved in various thermo-nuclear reactions.*

Reactions	Threshold Potential	Q in millimass	Q in Mev.	Q in K. cal per gm. $\times 10^{-7}$
$H^2+H^1 \rightarrow He^3+\gamma$	3·3 Kev.	5·742	5·349	3·9428
$H^2+H^2 \rightarrow He^3+n$		3·404	3·171	1·753
$H^2+H^2 \rightarrow H^3+H^1$	15 Kev.	4·26	3·97	2·1939
$H^3+H^1 \rightarrow He^4+\gamma$		21·32	19·683	10·979
$He^3+n \rightarrow He^4+\gamma$		22·18	20·665	11·42
$Li^7+H^1 \rightarrow 2He^4$	8 Kev.	18·54	17·00	4·76
$4H \rightarrow He^4+Q$		28·58	26·329	14·61
$Li^7+H^2 \rightarrow 2He^4+n$		15·91	14·81	3·63
$U^{235}+n \rightarrow {}_{x}A^{M}+ {}_{92-x}B^{M'}+2n$			180	1·8

known as the "Threshold Potential for the Reaction". For the lithium-proton reaction this has been found to be about 8 Kev. This quantity is not known with great precision yet.

The liberated energy can easily be calculated from the masses of the reactants. We have

Mass of Li^7	$= 7·01822$
Mass of H^1	$= 1·00812$
Sum	$= 8·02634$
Mass of 2 atoms of He	$= 8·00780$
Mass difference	$= 0·01854$

According to Einstein's law of equivalence of mass and energy this loss of mass reappears ultimately as kinetic energy of the products of the reaction corresponding to the law $\triangle E$ in ergs$=\triangle m.c^2$. Thus 1 millimass i.e. 0·001 times the mass of hydrogen corresponds to

$$\triangle E=1·60\times 10^{-20}.\ 10^{-3}.\ c^2 \text{ ergs} = 1·44\times 10^{-6} \text{ ergs}$$

$$=·91 \text{ Mev}=2·06\times 10^7 \text{ K. cal/gm-atom.}$$

With the aid of these relations, we can calculate the energy evolved either in millimasses, or in Mev or in kilocalories per gm-atom of nuclei consumed. These are shown in columns 3, 4, 5 respectively. Column (5) shows that when a gm-atom of Li^7-nucleus reacts completely with a gm-atom of protons producing 2 gm-atoms of helium nuclei, the total amount of energy liberated is $38 \cdot 2 \times 10^7$ K. cal i.e. $4 \cdot 76 \times 10^7$ K. cal per gram of the reactants.

Let us compare this figure with the energy evolved in a typical chemical reaction, e.g. the burning of coal. We have

$$C + O_2 = CO_2 + 98 \text{ K. cal.}$$

The energy produced is $98/44 = 2 \cdot 25$ K. cal per gm. of reactants, or $8 \cdot 1$ K. cal per gm. of carbon consumed. The energy produced in the $Li^7 + H^1 \rightarrow 2He^4$ reaction is 17 million times larger per gm. of the reactants, than we obtain per gm. of carbon in ordinary combustion. In other words, seven kilogrammes of Li and one kilogramme of hydrogen can give us by thermonuclear reactions as much energy as we can obtain by burning 46000 tons of coal.

The energy producing capacity of other nuclear reactions are also given for the sake of comparison in column 5.

Reaction (7) is the famous carbon cycle explained in greater detail later which according to Bethe and others, is responsible for the maintenance of the energy of the sun.

Reaction (9) represents fission of the Uranium nucleus, used for production of the Atom-Bomb. We see that the rate of energy-production is much less than in simpler nuclear reactions but we get by the fission of one kg. of U^{235} as much energy as by burning nearly 2500 tons of coal.

Sources of Stellar Energy.

The discovery of thermo-nuclear reactions has produced a fairly convincing solution of one of the outstanding problems in cosmology, viz. the source of stellar energy. Let us give an idea of this time-honoured problem. The sun which is a typical stellar body is emitting in the form of radiation $3 \cdot 78 \times 10^{33}$ ergs per sec. of energy, and since the mass of the sun is $1 \cdot 985 \times 10^{33}$ gm. we find it is producing 2 ergs of energy per sec. per gm. Geological evidence tells us that the sun has been giving out energy at this rate for at least 2 to 3 million years, which is the time of formation of the oldest form of rocks, viz. Archaeans. Actually, the age may be much higher. The total amount of energy radiated per gm. of solar matter within this time must be $> 2 \times 3 \times 10^7 \times 2 \times 10^9 > 1 \cdot 2 \times 10^{17}$ ergs, i.e. about $2 \cdot 6 \times 10^6$ K cal per gm. What is the process by which such huge amounts of energy are being produced? Further we have to remember that the sun is only one of billions of stellar bodies. The rate of emission of energy by other typical stellar bodies varies enormously, as table 14 shows.

Table 14.—*Emission of energy from different stars.*

Star	Spectral type	Mass	Density in gm./c.c.	Radius	Surface Temp. in °C.	Energy in erg./gm. sec.
Betelgeuse (α-Orionis)	M	40	2×10^{-5}	290	3000	300
Capella A	G	4·2	4×10^{-3}	11	5650	48
Capella B	F	3·3	$2{\cdot}8\times10^{-2}$	5·5	7400	41
V. Puppis	B	19·2	6×10^{-2}	7·6	22000	1100
H. D. 1337A	O	36·3	4×10^{-3}	23·8	28000	15000
Sirius A	A	2·45	·93	1·58	11200	29
Procyon A	F	1·13	·28	1·80	7000	10
Sun	G	1·00	1·42	1·00	6000	1·90
O_2 Eridani A	G	·90	3·7	·70	5600	·80
α-Centauri B	K	·97	·76	1·22	4400	·90
Kruger 60 A	M	·25	9·6	·33	3200	·068
60 B	M	·20	60·0	·17	,,	·021
Sirius B	A	·85	5×10^{4}	·03	8000	·007
Eridani B	A	·40	$9{\cdot}8\times10^{4}$	·018	11200	·002

[*Note.*—In the table the mass is in terms of the Sun as unity. Radius is given in terms of that of the Sun as unity. It may be noticed that rate of energy evolution is largest in case of giants, and least in the case of white dwarfs. The carbon cycle is responsible for the heat supply of the stars of main sequence. For giants, proton-proton reactions resulting in deuteron production is supposed to furnish the main heat supply.]

The first process which comes naturally to the mind is an exothermic chemical reaction like "Combustion" i.e. burning of carbon or carbon containing materials to CO_2. But the total amount of energy obtained in such processes, as we have already seen, is only of the order of a few K. cal per gm. So no ordinary chemical process can account for the source of stellar energy.

Helmholtz proposed that the energy may be derived from gravitational shrinkage of the stellar mass. He calculated that a shrinkage of a few hundred metres in its radius per year, would enable the sun to maintain its energy, but this is also insufficient in view of the time-scale for only 50 million years are required by the sun to shrink from infinite dispersal to the present state. So the problem remained an open one till the emergence of nuclear physics.

As we see from Table 14, there is enormous variation in the rate of production of energy by different stellar bodies. It is obvious that these variations must be due to differences in temperature, pressure and composition of different stellar bodies, and the details have to be worked out after careful weighing of all facts and observations relating to the particular star. For the stars of the main sequence, the main series of nuclear reactions which maintain the energy of the stellar body are believed to be the carbon cycle, postulated by Bethe in 1939. This is described in detail in the next paragraph.

The Carbon Cycle.

The Carbon Cycle consists of the following group of reactions :—

	Energy evolved	Half-life
$C^{12}+H^1 = N^{13}+\gamma$	2·0 Mev	
$N^{13} = C^{13}+\beta^{+}+\gamma$	0·5 Mev (3/8×1·4)	10·5 min.
$C^{13}+H^1 = N^{14}+\gamma$	8·2 Mev	
$N^{14}+H^1 = O^{15}+\gamma$	7·5 Mev	
$O^{15} = N^{15}+\beta^{+}+\gamma$	0·7 Mev (3/8×1·7)	2·1 min.
$N^{15}+H^1 = C^{12}+He^4$	5·2 Mev	
Total	24 Mev	

Four of the reactions are proton-reactions. The rest are β^{+} and γ emissions. It is seen that C^{12} which starts this chain of reactions, remains unchanged at the end of the cycle, the net result being the synthesis of four protons to a helium nuclei. C acts therefore as a catalyst only. In the graphic words of Prof. H. N. Russell : *Hydrogen forms the fuel and helium forms the ashes of the process of combustion which keeps the stars shining through ages.* The net energy evolved in one unit mechanism is 24·4 Mev or .6 Mev per gm. of proton gas converted. The β and γ rays which are emitted ultimately give up their energy to stellar matter. It is assumed that 7% of energy out of the gross amount evolved is carried away by the neutrinos, but even this may also ultimately be converted to energy by some process not yet known to us.

The rate at which the energy is evolved in this process depends upon physical conditions in the interior of stars, the concentration of protons and carbon. These have been worked out fully by Bethe and Critchfield, and can be found in the original sources, or in the *Theory of the Atomic Nucleus* by Gamow and Critchfield.

The Hydrogen Bomb.

Can such high temperature reactions be ever reproduced on the Earth? As we have seen they require a temperature of the order of a hundred million degrees.

This is no longer considered a fantastic dream after the production of the "Atom-Bomb." This, according to the available information, consists of lumps of uranium (235), or plutonium (239), weighing when assembled about 30 kg, and having a diameter of about 14 cm. When the pieces, which are normally kept apart, are assembled, the explosion takes place due to the fission of the atomic nuclei, and enormous amounts of energy are set free. The temperature of the exploding material can be shown to reach several hundred million degrees.

At these high temperatures other exothermic thermo-nuclear reactions may be started, for example, deuteron or lithium-hydrogen reactions. These highly exothermic reactions, once started, yield enough energy to maintain the high temperature and the thermo-nuclear reactions initiated may continue until the elements which cause the nuclear reactions are exhausted. The so-called 'hydrogen bomb' is probably such an arrangement where an "Atom Bomb" is detonated initially inside a mass of deuterium or lithium hydride initiating a highly exothermic thermo-nuclear reaction and yielding an enormous amount of energy which may be several hundred times more than the energy released in the explosion of an atom bomb.

Table 15 gives the occurrence of some ultrahigh temperatures and their probable energy sources.

Table 15.—*Some ultrahigh temperatures.*

Temp.	Occurrence	Source
2×10^4 °K	Surface of type O star	
3×10^5	Atomic-bomb fireball	atom bomb
1×10^6	Solar corona	
1×10^7	Solar interior	hydrogen thermo-nuclear reaction
1×10^8	Interior of some stars	helium thermo-nuclear reaction
2×10^9	Interior of hottest stars	oxygen thermo-nuclear reaction

18·22. Production of very high temperatures in the Laboratory.—We have seen above that ultrahigh temperatures of the order 10^7—10^9 exist in the interior of stars. Recently temperatures of the order 10^7—10^8 have been reached on our Earth by the hydrogen bomb. Attempts[1] have therefore been made in recent years to produce very high temperatures in the laboratory under controlled conditions and study various phenomena at these temperatures. At present these studies are of great interest to astronomers and aeronautical (or astronautical) engineers. They are however bound to become increasingly important in future for basic investigation and practical applications. By very high temperature we generally mean the region from 4000°C to 25000°C or more. At these high temperatures all matter is gaseous with energy high enough to produce considerable dissociation and ionization. The presence of large electron density can result in important long-range forces such as those leading to the phenomena of *magneto-hydrodynamics* and *plasma oscillations*. Due to these long-range forces high-temperature gas dynamics can show radical departures from ordinary gas dynamics. Such temperatures are usually produced by means of the shock tube.

The Shock Tube.

The construction of a shock tube is illustrated schematically in Fig. 13(a). It consists essentially of a high pressure and a low pressure chamber separated by a thin diaphragm. This diaphragm flattens against the tube walls very rapidly when the material is highly stressed by the high pressure and ultimately bursts producing a compression wave which travels to the right. Since the sound velocity $\mathscr{V}_0$ of small amplitude sound waves as well as the particle velocity u are greater in regions of higher density, it follows that in compression waves of finite amplitude the speed of the wave at any point a with respect to the wall which is $\mathscr{V}_a + u_a$, will be greater in the region of high pressure with the result that as the compression wave advances, regions of high pressure tend to overtake those of low pressure ahead of them ultimately making the front of the wave very steep. This steep front is called a shock front which moves into the low pressure gas and steepens as it advances. Simultaneously an expansion wave moves into the high pressure gas and broadens with time producing so-called expansion fan. In Fig. 13 (b) the waves created by the diaphragm burst can be traced in time while Fig. 13 (c) gives the pressure distribution along the tube at the instant of bursting t_0 and at a time t_1 later.

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[1] Recently (Jan. 24, 1958) the British and the United States scientists have announced that they have succeeded in producing, in a plasma of deuterium gas, temperatures as high as 5 million °C by passing an electric current of the order 10^5 amperes through it and had maintained these temperatures for a few thousandths of a second. The Harwell apparatus accomplishing this is known as Zeta (Zero Energy Thermonuclear Assembly).

The surface separating the two gases which were originally present in the high and low pressure portions of the shock tube is called

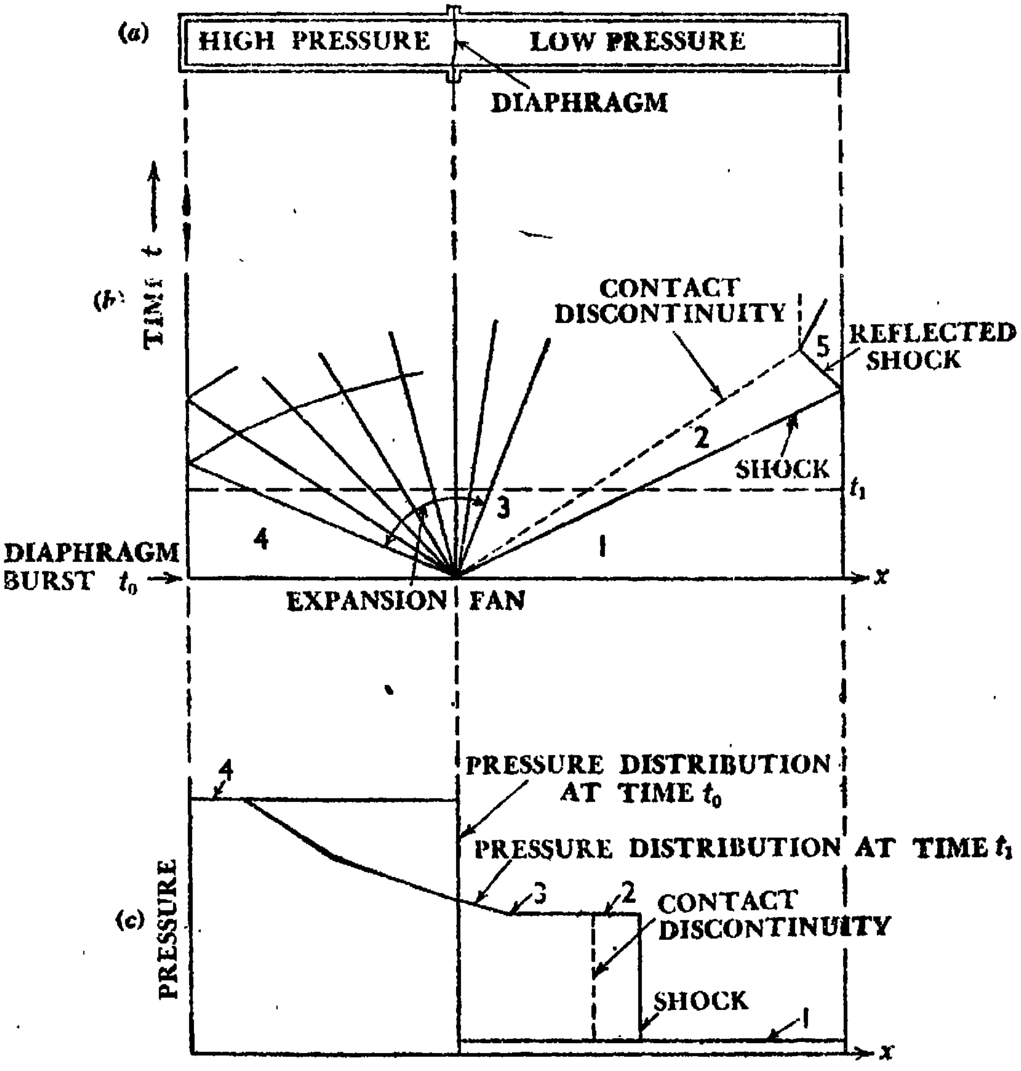

Fig. 13.—Schematic representation of the shock tube and the wave progression.

the contact discontinuity. We distinguish two types of discontinuity surfaces—*contact surfaces* and *shock fronts.* Contact surface or discontinuity is a surface separating two parts of the medium without any flow of gas through the surface. Thus the pressure p and the particle velocity u are the same in regions 2 and 3 though the gases are different. Shock front is a surface discontinuity which is crossed by the gas. Thus p and u are different in regions 1 and 2 but the gas is the same. The shock front always moves with supersonic speed as observed from the front side and with subsonic speed as observed from the back side. The zone of flow behind a shock front is called a shock wave.

The equations applying to the shock front were developed by Rankine and by Hugoniot from the principles of conservation of mass, momentum and energy across the front. These equations enable us to determine the shock velocity U_s and the particle velocity u in terms of the pressure and density on the two sides of the front. It is evident that the rapid compression of the fluid within the shock wave will produce, on account of dissipative forces, a much higher temperature than mere adiabatic compression. Detailed considerations[1] show that if the gas 1 is a perfect gas with constant heat capacity, the temperature ratio T_2/T_4 for the limiting case when $p_4/p_1 \rightarrow \infty$ is given by

$$\frac{T_2}{T_4} \cong \frac{\gamma_4 (\gamma_1 - 1)}{2\gamma_1} \left(\frac{\gamma_1 + 1}{\gamma_4 - 1} \right)^2 \frac{\mu_1}{\mu_4}, \quad . \quad . \quad . \quad (58)$$

where γ is the ratio of the two specific heats and μ is the molecular weight. Thus the temperature T_2 attained in the shock will be increased by increasing the temperature of the driver gas, decreasing its molecular weight, and increasing the molecular weight of the driven gas. For these reasons hydrogen is chosen as driver gas which is usually heated by internal combustion or electrical discharge. Using argon as the driven gas and ignoring ionisation $T_2/T_4 \cong 250$. Due to reflection of this shock from the closed end of the low pressure chamber on the right the temperature is further increased in region 5. In this way temperatures upto 18000°K have been attained. At these high temperatures the gas becomes very much ionised and is highly conducting, a filament of the gas behaving like a wire in an electric or magnetic field. The maximum possible shock Mach number $(M \equiv U_s/\mathcal{V}_1)$ i.e. the ratio of the shock velocity to the velocity of sound ahead of the shock, is given by

$$M_\infty = \frac{\gamma_1 + 1}{\gamma_4 - 1} \frac{\mathcal{V}_4}{\mathcal{V}_1} \quad . \quad . \quad . \quad . \quad . \quad (59)$$

Thus to produce strong shocks $\mathcal{V}_4/\mathcal{V}_1$ must be large i.e. the driver gas must be as light and at as high temperature as possible.

The shock tube components are shown in Fig. 14. At the left end of the tube is a short section which is filled with hydrogen separated from it by a heavy copper diaphragm. There is in the centre of the tube a long section, part of which is glass containing argon gas at a pressure of 1 cm. When the hydrogen is exploded with a spark plug, the diaphragm breaks and the expanding high pressure gas acts like a piston pushing the low-pressure gas ahead of it. Thus a shock wave rushes through the argon from left to right travelling at about 4/3 times the piston velocity. When the shock is sufficiently intense the gas becomes luminous and is examined spectroscopically with the help of a grating and a rotating drum camera. At the far right is a second diaphragm which is broken by the shock wave and thereby prevents the wave from being reflected back down the tube and break the glass tube. In this way shocks of $M=17$ were produced in argon, the resulting temperature being about 18000°C, and about 40% of argon being ionized.

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[1] For details see Resler, Lin and Kantrowitz, *J. App. Phys.* **12**, 1390, 1952.

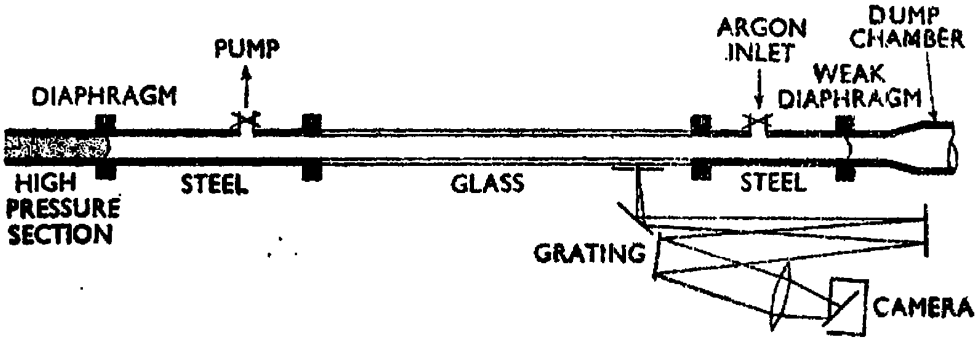

Fig. 14.—The experimental shock tube.

When high temperatures are produced in the laboratory we must have materials to contain and survive those temperatures. Ordinary metals and alloys melt but molybdenum, tungsten, tantalum and columbium have high melting points though Mo is exceedingly sensitive to

Table 16.—*Materials for high temperature work.*

Material	Service Limit °C.	Melting Point °C.
Super alloys	850	..
Molybdenum alloys	1000	..
Cermets	1250	..
Iron	..	1533
Silica	..	1720
Alumina (Al_2O_3)	..	1900
Silicon Carbide (SiC)	..	2300
Fused Magnesia (MgO)	..	2620
Zirconium boride (ZrB_2)	..	3060
Titanium Carbide (TiC)	..	3140
Fused Thoria (ThO_2)	..	3300
Tungsten	..	3380
Zirconium Carbide (ZrC)	..	3540
Hafnium Carbide	..	4000

oxidation at high temperatures. Ceramics which are metals in combination with other elements (e.g. O, C, B) have very high melting points but are very brittle. During the last ten years, however, promising new types of ceramics have been developed—the metallic oxides, carbides, nitrides, borides or silicides, the most important being titanium carbide and zirconium boride. Ceramic oxides entirely avoid the problem of oxidation but are sensitive to thermal shock, while the others are susceptible to oxidation. Attempts are being made to combine the good mechanical properties of metals with the chemical inertness of the ceramics by making combinations of ceramics and metals—the so-called cermets. Table 16, p. 843 will enable a choice of materials to be made for containment of heat. Cooling techniques make it possible to contain much higher temperatures.

BOOKS RECOMMENDED

1. Planck—*Treatise on Thermodynamics.*
2. Jellinek—*Lehrbuch der physikalischen Chemie*, Band II & III.
3. Eucken—*Lehrbuch der Chemischen Physik.*
4. Glasstone—*Theoretical Chemistry.*
5. Fowler and Guggenheim—*Statistical Thermodynamics.*
6. G.S. Rushbrooke—*Introduction to Statistical Mechanics* (Clarendon Press, Oxford, 1949).
7. W. C. Band—*Introduction to Quantum Statistics* (Van Nostrand Co., 1955).

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For application of the theory of thermal ionisation to the various spectra of the sun and of stars, See Unsold, *Physik der Stern-atmosphere*; also Abbot, *The Sun*; S. Rosseland, *Theoretical Astrophysics.*

For the chemical composition of the Solar Atmosphere, see Russell, Molecules in the sun and the stars, *Ap. J.*, **79**, 317; Sitterley, *Proc. Am. Phil. Society*, **81**, 125; Strömgren, On the Chemical Composition of the Solar Atmosphere, *Strömgren Festschrift*, 1940, and other papers in current physical and astronomical journals.

For shock waves and high-temperature gas dynamics see Courant and Friedrichs, *Supersonic Flow and Shock Waves* (1948); Spitzer, *Physics of Fully Ionized Gases* (1956); Cowling, *Magnetohydrodynamics* (1957), Interscience Publishers; Cole, *Underwater Explosions* (1948), Princeton University Press.

APPENDIX

NOTE 1

Proof of Maxwell's theorem that when two types of molecules continually collide the mean kinetic energy of each type ultimately becomes the same.

Let us consider the collision of two perfectly elastic spheres of masses M and m, moving in *opposite* directions with velocities AP and BQ varying inversely as their masses. If P and Q (Fig. 1) be the centres of these spheres, the motion of the spheres before and after impact will be as shown in the figure. It can be easily seen from the laws of impact that the velocities along the line of centres will be reversed in sign while that perpendicular to it will remain unchanged. Hence the directions of motion of each sphere after impact will make the same angle with the line of centres as they made before the impact. We shall use this result to find the motion of two molecules (assumed to be spherical) after impact.

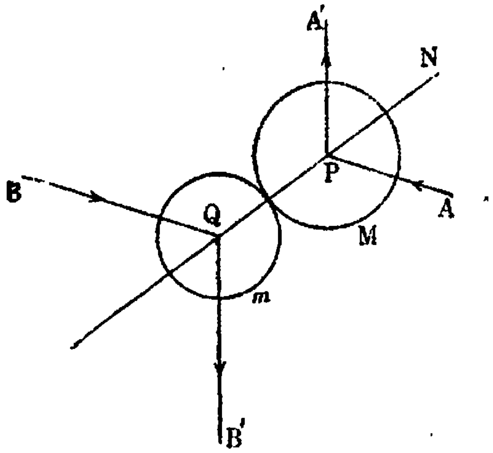

Fig. 1.

We make the following geometrical construction. Let OA and OB (Fig. 2) represent the velocities before impact of two molecules, one taken from each type of gas. These velocities can have in general any magnitude and direction. AB is the mutual relative velocity of the molecules. Had there been no action between the molecules they would have been at A and B after one second. Take a point G in AB such that $M.\,AG = m.\,BG$ *i.e.*, G is the centre of gravity of the two molecules. OG represents the velocity of the centre of gravity and GA and GB the relative velocities of the molecules with respect to the centre of gravity. Now it follows from the law of conservation of momentum that the motion of G is not affected by the mutual action of the molecules and hence G continues its path in space quite unaffected by the collision. Draw a line GN in space parallel to the line of centres at impact of the two molecules. Now, since the two molecules were moving initially with velocities, relative to G, of the magnitudes GA and GB,

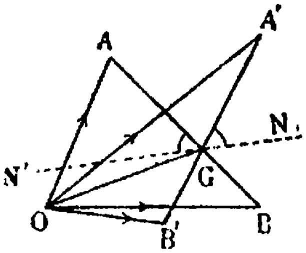

Fig. 2.

i.e., with velocities inversely as their masses and directed oppositely, it follows from the result established above that after impact the position of each molecule will be symmetrical about the line of centres GN with its initial position, *i.e.*, ∠AGN′ = ∠A′GN and AG = A′G. Similarly ∠BGN = ∠B′GN′ and BG = B′G. Thus GA′ and GB′ will represent the velocities of the molecules after the impact relative to G and OA′ and OB′ the new absolute velocities after impact.

In the whole gas there are molecules moving with all velocities. Let us fix our attention on a molecule of the first gas. It is surrounded by molecules of the second gas having all velocities in all directions, which are symmetrically distributed in space. Thus OA and OB can make all angles; we can therefore take the mean value which will be a right angle. Thus we can represent by the arms of a right angle OAB (Fig. 3) one molecule of each type of gas having the mean velocities $\bar{v}_1$, $\bar{v}$; *i.e.*, OA $= \bar{v}_1$, OB $= \bar{v}$. The mean[1] relative velocity of the type of molecules is $\sqrt{\bar{v}_1^2+\bar{v}^2}$, and the mean velocity of the centre of gravity is OG, where AG : BG = $m : M$. After impact the mean relative velocity of the two types about the centre of gravity is given by GA′ and GB′ where the line A′GB′ is perpendicular to OG, and A′G = AG; B′G = BG. This is because, as proved above, the relative velocity about G, *viz.*, GA′ can have all directions depending upon the direction of the line of centres at impact; the mean value of the angle which these directions make with OG is a right angle. Hence OA′ and OB′ represent the mean velocities $\bar{v}_1'$ and $\bar{v}'$ after impact. Hence

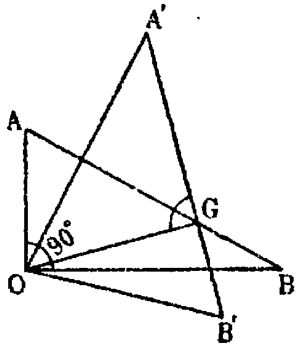

Fig. 3.

$$\mathrm{AB} = \sqrt{\bar{v}_1^2+\bar{v}^2}, \quad \mathrm{AG} = \frac{m}{m+M}\sqrt{\bar{v}_1^2+\bar{v}^2}$$

$$\mathrm{BG} = \frac{M}{M+m}\sqrt{\bar{v}_1^2+\bar{v}^2}$$

$$\mathrm{OG}^2 = \mathrm{AG}^2+\mathrm{AO}^2-2\mathrm{AG}.\,\mathrm{OA}.\,\frac{\mathrm{OA}}{\mathrm{AB}}$$

$$= \frac{m^2}{(M+m)^2}(\bar{v}_1^2+\bar{v}^2)+\bar{v}_1^2-2\frac{m}{M+m}\sqrt{\bar{v}_1^2+\bar{v}^2}.\ \frac{\bar{v}_1^2}{\sqrt{\bar{v}_1^2+\bar{v}^2}};$$

or

$$\mathrm{OG} = (M^2\bar{v}_1^2 + m^2\bar{v}^2)^{\frac{1}{2}}/(M+m)$$

and

$$\bar{v}_1' = \mathrm{OA}' = \sqrt{\mathrm{OG}^2+\mathrm{GA}^2} = \{M^2\bar{v}_1^2+m^2\bar{v}^2+m^2(\bar{v}_1^2+\bar{v}^2)\}^{\frac{1}{2}}/(M+m)$$

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[1] This can be proved more rigorously. See Maxwell, *Collected Works* Vol. I, pp. 382-383.

kind of collision, to be herewith designated as a collision of α-class, which is such that it satisfies the following three conditions :—

(1) One of the two colliding molecules belongs to A-type.

(2) The second colliding molecule belongs to the B-type (the B-type is defined to be such as has its velocity components in the intervals u', $u'+du'$, v', $v'+dv'$, w', $w'+dw'$).

(3) We restrict ourselves to only those collisions in which at the instant of impact, the line joining the centre of A-molecule to the centre of B-molecule has a definite orientation in space. This is such that the direction from A to B has the direction cosines lying between l and $l+dl$, m and $m+dm$, n and $n+dn$ and thus subtends a small finite solid angle $d\omega$. This small finite solid angle has to be assumed because the direction of the line of centres varies within certain small limits on account of the velocity intervals du, dv, dw and du', dv', dw' for the two types of molecules.

The number of molecules of class A is $nf(u, v, w)\, du\, dv\, dw$ per unit volume and each of these can suffer a collision of the α-class. Imagine a concentric sphere of radius σ described about the centre of each of these A-molecules (σ = molecular diameter). Then for a collision of the α-class, the centre of a molecule of the B-type must lie on the surface of this sphere at the moment of impact and must be further contained in a small area $\sigma^2 d\omega$ of the surface with the line of centres in the direction l, m, n. Before the instant of collision, the B-molecule must be moving relative to A with the velocity c_r of which the components are $u'-u$, $v'-v$, $w'-w$, *i.e.*, in a direction λ, μ, ν (Fig. 1) such that

$$\lambda = \frac{u'-u}{c_r}, \quad \mu = \frac{v'-v}{c_r}, \quad \nu = \frac{w'-w}{c_r}. \qquad (1)$$

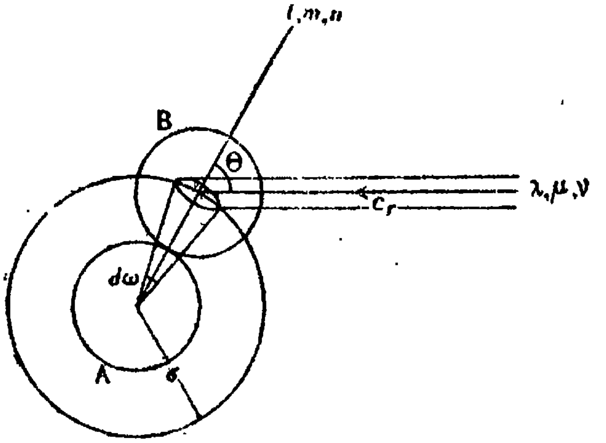

Fig. 1

Hence all those molecules of B-type suffering collision of the α-class with this single A-molecule in time dt are contained in the oblique cylinder of base $\sigma^2 d\omega$ and slant height $c_r dt$, the axis of the cylinder being inclined to the normal to the base at an angle θ such that

$$\cos\theta = -(l\lambda + m\mu + n\nu) \qquad (2)$$

The volume of the cylinder is thus $c_r\,dt\,\sigma^2\,d\omega\cos\theta$ and the number of B molecules contained therein is $nf(u', v', w')\,du'\,dv'\,dw'\,c_r\cos\theta\,\sigma^2\,d\omega dt$. This represents the number of collisions with this single A-molecule. But there are $n\,f(u, v, w)\,dudvdw$ molecules per c.c. of the A-type. Hence the total number of collisions of the α-type per c.c. between A-molecules on the one hand and B on the other in time dt is

$$n^2 f(u, v, w)\,f(u', v', w')\;c_r\;\cos\;\theta\;\sigma^2 d\omega\;du\,dv\,dw\,du'\,dv'\,dw'\,dt. \qquad (3)$$

This gives the required decrease in the number of A-molecules by collisions of the α-class.

We shall next find the number of A-molecules produced in the time dt by collision with other molecules. We shall now consider collisions of a type, to be herewith designated as collisions of the β-class, which satisfy the following three conditions :—

(1) After collision one of the colliding molecules belongs to A-type.

(2) After collision the other colliding molecule belongs to B-type.

(3) The direction of the line of centres at impact satisfies the same condition as in collisions of α-class.

We can easily find from the laws of elastic impact as to what are the initial velocities of the molecules before collision which, after suffering the β-collision produce the A- and B-molecules. We know that during elastic collisions the two spheres interchange their velocities along the line of centres while the components in the perpendicular direction remain unaffected. Let us denote the velocity components of the two types of molecules which on suffering a β-collision produce the A- and B-molecules by $\overline{u}, \overline{v}, \overline{w}$ and $\overline{u'}, \overline{v'}, \overline{w'}$ respectively, the resultant velocities being $\overline{c}$ and $\overline{c}'$. The resultant velocities after impact are c and c'. Denoting the component of the velocity along the line of centres by the suffix n, and that perpendicular to it by t, and expressing *vectorially*, we have

$$\begin{aligned}\overline{c}&=\overline{c}_t+\overline{c}_n=c_t+c_n{}'=c-c_n+c_n{}'\\&=c+(c'-c)_n=c+(c_r)_n \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)\end{aligned}$$

and

$$\begin{aligned}\overline{c'}&=\overline{c_t'}+\overline{c_n'}=c_t{}'+c_n=c'-c_n{}'+c_n\\&=c'-(c'-c)_n=c'-(c_r)_n \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)\end{aligned}$$

since

$$c_t=\overline{c}_t,\; c_t{}'=\overline{c_t'},\; c_n=\overline{c_n'},\; c_n{}'=\overline{c}_n$$

$c_r=c'-c$ = relative velocity after a collision of β-class.

The relative velocity after impact in β-collision is the same as the relative velocity before impact in α-collision. Hence

$$(c_r)_n = l(u'-u)+m(v'-v)+n(w'-w).$$

Equations (4) and (5) can now be written in terms of the three components. Then we get

$$\bar{u} = u + l(c_r)_n = u - [l^2(u-u') + lm(v-v') + ln(w-w')], \quad . \qquad . \quad (6)$$

and $$\bar{u}' = u' - l(c_r)_n = u - [l^2(u'-u) + lm(v'-v) + ln(w'-w)] \, . \qquad . \quad (7)$$

There will be similar expressions for $\bar{v}$, $\bar{v}'$, $\bar{w}$, $\bar{w}'$.

In analogy with the preceding case of α-collisions, it follows that the number of impacts between these molecules ($\bar{u}$, $\bar{v}$, $\bar{w}$; $\bar{u}'$, $\bar{v}'$, $\bar{w}'$) per unit volume in time dt, the collisions being such that A- and B-types are formed, is

$$n^2 f(\bar{u}, \bar{v}, \bar{w}) f(\bar{u}', \bar{v}', \bar{w}') \, d\bar{u} \, d\bar{v} \, d\bar{w} \, d\bar{u}' \, d\bar{v}' \, d\bar{w}' \, \sigma^2 \, c_r \cos\theta \, d\omega \, dt \quad . \quad (8)$$

These collisions will all belong to β-class only when the limits of $d\bar{u}$, $d\bar{v}$ .... are such that the values of u, v .... as determined by equations (6) and (7) lie within the limits u, $u+du$, v, $v+dv$ ... etc. To obtain the total number of β-collisions we must integrate expression (8) for such values of du, dv....

Let us consider the product $d\bar{u} \, d\bar{v} \, d\bar{w} \, d\bar{u}' \, d\bar{v}' \, d\bar{w}'$. It can be shown by substituting the values of u, v, w.... etc. in terms of u, v... from (6) and (7) that

$$d\bar{u} \, d\bar{v} \, d\bar{w} \, d\bar{u}' \, d\bar{v}' \, d\bar{w}' = du \, dv \, dw \, du' \, dv' \, dw'.$$

This is simply a particular case of the famous Liouville's theorem. We can therefore substitute this value in (8).

The total number of molecules of class A which are formed in time dt by collisions will be obtained by integrating expression (8) for all values of u', v', w' and over all possible values of $d\omega$. Similarly the total number of molecules of class A which disappear on account of collisions will be obtained by integrating expression (3) through the same range of values. Hence the net increase in the A-type of molecules in time dt is

$$n^2 \, du \, dv \, dw \iiiint (\bar{f} \bar{f}' - f f') \, c_r \, \sigma^2 \cos\theta \, du' \, dv' \, dw' \, d\omega,$$

where $f, f', \bar{f}, \bar{f}'$ are written for $f(u, v, w)$, $f(u', v', w')$, $f(\bar{u}, \bar{v}, \bar{w})$ and $f(\bar{u}', \bar{v}', \bar{w}')$ respectively.

Now the number of A-molecules per c.c. at the beginning of the interval was $n \, f \, du \, dv \, dw$. Hence the gain in time dt will be given by

$$n \frac{\partial f}{\partial t} \, dt \, du \, dv \, dw,$$

since n is constant. Equating this to the above expression for increase of A-molecules, we get

$$\partial f / \partial t = n \iiiint (\bar{f} \bar{f}' - f f') \, c_r \, \sigma^2 \cos\theta \, du' \, dv' \, dw' \, d\omega, \quad . \qquad . \quad (9)$$

The condition for a steady state is that $\partial f/\partial t = 0$, *i.e.*, the integral on the right should vanish. This may be possible in two ways :—(1) $\bar{f}\,\bar{f}' - f f' = 0$; (2) the integral taken within the limits may vanish as a whole.

Now it will be shown that for the elastic collisions considered the quantity $\bar{f}\bar{f}' - ff'$ is either always negative or zero so that the integral as a whole can never vanish unless $\bar{f}\bar{f}' - ff'$ is itself zero for θ is always less than $\pi/2$ and $\cos\theta$ is therefore positive. Hence the condition $\bar{f}\bar{f}' - ff' = 0$ is *sufficient* and at the same time *necessary* for equilibrium. The proof of this important result was first given by Boltzmann by introducing his H function which is defined by

$$H = \int\int\int f \log f \, du\, dv\, dw, \qquad (10)$$

where the integration extends over all possible values of u, v, w. It may be pointed out that merely from the result $df/dt = 0$ it is not possible to deduce the condition *necessary* for equilibrium. Of course it readily follows that $\bar{f}\bar{f}' - ff' = 0$ is a sufficient condition for equilibrium.

THE H-FUNCTION

From the definition of the quantity H by means of Eq. (10) it follows that H is a pure number and is not a function of u, v, w. It depends entirely upon the function f which determines the law of distribution of velocities. Hence as long as f remains unchanged, H also does not change; in other words, the condition $\partial f/\partial t = 0$ is synonymous with the condition $\partial H/\partial t = 0$. Hence the condition of equilibrium is given by

$$\partial H/\partial t = 0.$$

Differentiating equation (10) with respect to t, we get

$$\frac{\partial H}{\partial t} = \iiint (1 + \log f)\frac{\partial f}{\partial t}\, du\, dv\, dw.$$

Substituting in this the value of $\partial f/\partial t$ from (9) we get

$$\frac{\partial H}{\partial t} = n \int\int\int\int\int\int\int (1 + \log f)\,(\bar{f}\,\bar{f}' - ff')\, c_r \sigma^2 \cos\theta \; du\, dv\, dw\, du'\, dv'\, dw'\, d\omega. \qquad (11)$$

We have obtained the above equation by considering the increase and decrease of the A-type of molecules. Had we started with the B-type of molecules, we would have got

$$H = \int\int\int f' \log f' \; du'\, dv'\, dw',$$

and

$$\frac{\partial H}{\partial t}=\iiint(1+\log f')\frac{\partial f'}{\partial t}\,du'\,dv'\,dw',$$
$$=n\int\int\int\int\int\int\int(1+\log f')(\bar{f}'\bar{f}-f'f)\,c_r\,\sigma^2\cos\theta$$
$$du\;dv\;dw\;du'\;dv'\;dw'\;d\omega,$$

which is obtained simply by rewriting equation (11) in such a way that the accented letters are merely substituted for the unaccented and *vice versa*. Adding these two expressions for $\partial H/\partial t$ and dividing by 2 we get the average value of $\partial H/\partial t$ in which both types of molecules A and B are regarded equally. This yields

$$\frac{\partial H}{\partial t}=\frac{1}{2}n\int..\int(2+\log ff')(\bar{f}\bar{f}'-ff')\,c_r\,\sigma^2\cos\theta\,du\,dv\,dw\,du'\,dv'\,dw'\,d\omega.\quad(12)$$

In deducing this result the typical class of collision was taken to be the collision of the α-class. If however in place of the α-collision, we consider the β-collision to be typical, *i.e.*, the one in which the initial velocities are $\bar{u}$, $\bar{v}$, $\bar{w}$, $\bar{u}'$, $\bar{v}'$, $\bar{w}'$, and the final velocities are u, v, w, u', v', w', we get

$$\frac{\partial H}{\partial t}=\frac{1}{2}n\iiiint\!\!\iiint(2+\log\bar{f}\;\bar{f}')(ff'-\bar{f}\bar{f}')\,c_r\,\sigma^2\cos\theta$$
$$d\bar{u}\,d\bar{v}\,d\bar{w}\,d\bar{u}'\,d\bar{v}'\,d\bar{w}'\,d\omega\quad.\quad(13)$$

which is obtained simply by interchanging the dashed and undashed letters in (12). The differential product $d\bar{u}\,d\bar{v}\,d\bar{w}\,d\bar{u}'\,d\bar{v}'\,d\bar{w}'$ in (13) can be replaced by $du\,dv\,dw\,du'\,dv'\,dw'$ as already proved.

Combining these two values of $\partial H/\partial t$, we get a neutral value of $\partial H/\partial t$ in which the A- and B-molecules and the α and β collisions have all been equally regarded. Hence finally we get the expression

$$\frac{\partial H}{\partial t}=\frac{1}{4}n\iiiint\!\!\iiint(\log ff'-\log\bar{f}\bar{f}')(\bar{f}\bar{f}'-ff')\,c_r\,\sigma^2\cos\theta$$
$$du\;dv\;dw\;du'\;dv'\;dw'\;d\omega\quad.\quad.\quad(14)$$

Now whether ff' is greater or less than $\bar{f}\bar{f}'$ the quantities $(\log ff'-\log\bar{f}\bar{f}')$ and $\bar{f}\bar{f}'-ff'$ will have opposite signs and hence their product will always be negative. Now since $c_r\cos\theta$ is always positive, the integral can never vanish unless $\bar{f}\bar{f}'-ff'=0$. Hence the condition

$$\bar{f}\bar{f}'-ff'=0,\quad.\quad.\quad.\quad.\quad(15)$$

is sufficient as well as necessary for equilibrium.

The solution of equation (15) will give the distribution law in the steady state. To solve it, let us take logarithms. We get

$$\log f+\log f'-\log \bar{f}-\log \bar{f'} = 0. \qquad (16)$$

Let us assume that the solution of the equation is of the form

$$f = e^{\phi(c^2)}.$$

On substituting such values of $f, f', \bar{f}, \bar{f'}$ in (16) we get

$$\phi(c^2)+\phi(c'^2)-\phi(\overline{c^2})-\phi(\overline{c'^2}) = 0, \qquad (17)$$

where the c's are connected by the relation

$$c^2+c'^2 = \overline{c^2}+\overline{c'^2}.$$

Hence (17) yields

$$\phi(c^2)+\phi(c'^2) = \phi(\overline{c^2})+\phi(c^2+c'^2-\overline{c^2}).$$

Differentiating this with respect to c^2, c'^2, $\bar{c}^2$, respectively, we get

$$\phi'(c^2) = \phi'(c'^2) = \phi'(\overline{c^2}) = \phi'(c^2+c'^2-\overline{c^2}). \qquad (18)$$

This can be satisfied only when each of these is equal to a constant, *i.e.*

$$\phi'(c^2) = \text{constant} = -1/a^2 \text{ (say)}.$$

Hence
$$\phi(c^2) = -c^2/a^2 + \log A^3,$$

where $\log A^3$ is a constant of integration. Hence

$$f = A^3 e^{-c^2/a^2}$$

or
$$f(u, v, w) = A^3 e^{-\frac{1}{a^2}(u^2+v^2+w^2)}$$

and
$$f(u) = A e^{-u^2/a^2}$$

which is Maxwell's distribution law.

BOLTZMANN'S *H*-THEOREM

We have proved above that the quantity $\partial H/\partial t$ always remains negative. In the state of equilibrium alone it is zero, while it is never positive, *i.e.*

$$\frac{\partial H}{\partial t} \leqq 0.$$

In other words the mechanical quantity H defined above is such a function of the system that it always decreases in natural processes while in the limiting case of equilibrium it remains constant. This is known as Boltzmann's H-theorem. The student will remember having come across the entropy function S in the study of thermodynamics which is such that it always increases, but during equilibrium it remains constant, *i.e.*

$$\frac{dS}{dt} \geqq 0.$$

$$\bar{c}' = \mathrm{OB}' = \sqrt{\mathrm{OG}^2+\mathrm{GB}^2} = \{ M^2\bar{c}_1{}^2+m^2\bar{c}^2+M^2(\bar{c}_1{}^2+\bar{c}^2) \}^{\frac{1}{2}}/(M+m)$$

$$M\bar{c}_1{}'^2 - m\bar{c}'^2 = \left(\frac{M-m}{M+m}\right)^2 (M\bar{c}_1{}^2 - m\bar{c}^2).$$

Thus the difference in kinetic energy of the two types of molecules after impact is less than that before it. Hence after a large number of impacts the difference will be vanishingly small and may be put equal to zero. We would then have

$$M\bar{c}_1{}'^2 = m\bar{c}'^2, \quad \text{or} \quad M\bar{c}_1{}^2 = m\bar{c}^2,$$

i.e., the mean kinetic energy of each type becomes the same and there will be no more exchange. When there is no exchange of energy we say that the gases are at the same temperature. Hence the equality of temperature implies that the mean kinetic energy of both types is the same, *i.e.*, temperature is a measure of the mean kinetic energy of the molecules.

NOTE 2

Deduction of Maxwell's Law of Distribution of Velocities by the Method of Collisions[1]

If in the steady state a law of distribution of velocities holds which does not change with time, it is evident that this distribution law should follow from the condition that the number of molecules having velocities lying between certain limits is not altered by the elastic impact of molecules with one another. We shall now mathematically discuss the consequences of this condition. For simplicity the molecules are supposed to be rigid elastic spheres.

Consider one set of molecules whose velocity components lie between the limits u, $u+du$, v, $v+dv$, w, $w+dw$. Their number per unit volume may be denoted by $n\,f(u, v, w)\,du\,dv\,dw$ where n is the molecular density. For brevity, we shall designate them as molecules of the A type. Now since the velocity of a molecule remains constant except when collisions take place it is evident that molecules can *enter* or *leave* class A only through the occurrence of collisions. In the steady state the equilibrium must exist between these two changes so that the net change in the number of A-molecules is zero. This condition of no change determines the law of distribution.

We may begin by considering those collisions by which the A-type of molecules are decreased in number. Let us consider a special

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[1] The treatment given here is largely taken from Jeans's *Dynamical Theory of Gases.*

Thus it will be seen that the function H is closely related to negative entropy. In fact it can be shown that

$$S = -kH,$$

where k is Boltzmann's constant. It is shown in the chapter on Statistical Thermodynamics that

$$S = k \log W,$$

where W is the thermodynamic probability of the system. Hence we get

$$H = -\log W,$$

which gives the relation between H and the thermodynamic probability of the system.

NOTE 3

Definite Integrals used in the Kinetic Theory of Gases

The following definite integrals occur very frequently in the Kinetic Theory of Gases and the student should be able to reproduce them:—

$$\int_0^\infty e^{-bu^2}\,du = \frac{1}{2}\sqrt{\frac{\pi}{b}}, \qquad \int_0^\infty e^{-bu^2}\,u\,du = \frac{1}{2b},$$

$$\int_0^\infty e^{-bu^2}\,u^2du = \frac{1}{4}\sqrt{\frac{\pi}{b^3}}, \qquad \int_0^\infty e^{-bu^2}\,u^3du = \frac{1}{2b^2}.$$

$$\int_0^\infty e^{-bu^2}\,u^4du = \frac{3}{8}\sqrt{\frac{\pi}{b^5}}. \qquad \int_0^\infty e^{-bu^2}\,u^5du = \frac{1}{b^3}.$$

Each integral can be obtained by differentiating the one just above it with respect to $-b$. In this way the system can be extended indefinitely. If the limit extends from $-\infty$ to $+\infty$, the above values have to be doubled for even powers of u while they reduce to zero for odd powers of u.

It will be seen that the foregoing formulae are simply particular cases of the general formulae

$$\int_0^\infty e^{-bu^2}\,u^{2k}du = \frac{1\,.\,3\,.\,\ldots\,.\,(2k-1)}{2^{k+1}}\sqrt{\frac{\pi}{b^{2k+1}}}.$$

$$\int_0^\infty e^{-bu^2}\,u^{2k+1}du = \frac{k\,!}{2b^{k+1}}$$

NOTE 4

Experimental proof of Maxwell's Distribution Law from the Finite Breadth of Spectral Lines

As explained on p. 139 every spectral line has a finite width because of the fact that the vibrating atom is not at rest but is moving with large velocities and consequently the frequency changes on account of Döppler effect. We can calculate this width mathematically as follows:—

Let ν_0 be the frequency of light emitted by a particle at rest. Now the particles in the vacuum tube are not at rest. According to the kinetic theory they are moving to and fro, the distribution of velocities being given by Maxwell's Law. If a particle is approaching the observer with the component velocity u, the frequency becomes $\nu_0(1+u/c)$. If it is going away from the observer, the frequency becomes $\nu_0(1-u/c)$. As 'u' has all values from 0 to ∞, the line will have all frequencies about a central value ν_0 *i.e.*, theoretically it will be of infinite breadth. But as we know from Maxwell's theory, particles with very large velocities are extremely rare; hence the intensity due to them will be extremely small. The distribution of intensity in the line can be obtained as follows :—

Let dn be the number of particles having their velocity components in the line of vision between u and $u+du$. Then we have

$$dn = n_0 a e^{-\frac{mu^2}{2kT}} du$$

where a is a constant.

The frequency of light emitted by such particles is $\nu_0(1\mp u/c)$, and the intensity I is proportional to the number of particles. Hence

$$I = I_0 e^{-\frac{mu^2}{2kT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where I_0 is the intensity in the centre. We shall now convert this into a convenient form. Let λ_0 denote the wavelength of the central line, then $\lambda_0 = c/\nu_0$.

Let $\lambda_0 - x$ correspond to the frequency $\nu_0(1+u/c)$. Then

$$\lambda_0 - x = \frac{c}{\nu_0(1+u/c)} = \frac{c}{\nu_0}\left(1 - \frac{u}{c}\right) = \lambda_0 - \frac{u}{\nu_0}.$$

Thus

$$x = \frac{u}{\nu_0} = \lambda_0 \frac{u}{c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Then I_x, the intensity at a distance x from the centre (x being measured in wavelength units) is given by

$$I_x = I_0 e^{-\beta x^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\beta = \frac{1}{2} m\nu_0^2/kT$.

Hence the distribution of intensity in the line about the centre will follow a probability curve (Fig. 1). We can now define a half-width.

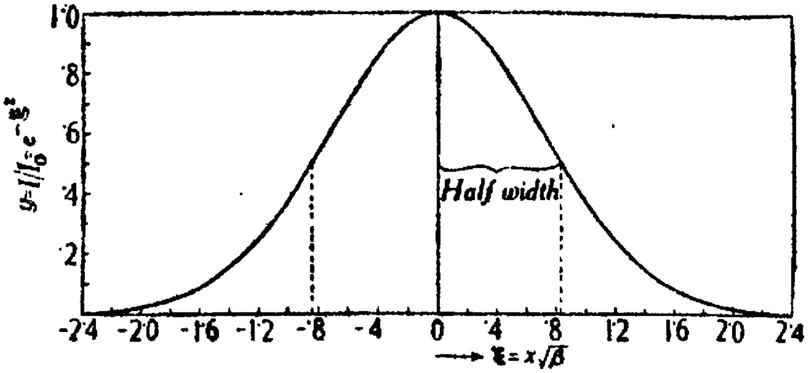

Fig. 1.—Distribution of intensity in a spectral line.

Let 'b' be the distance on the wavelength scale on either side where $I_x = \frac{1}{2} I_0$. Then b = half-width. We have from (3)

$$\frac{I_0}{I_x} = e^{\beta b^2} = 2, \quad \text{hence } b^2 = \frac{ln\ 2}{\beta},$$

or

$$b^2 = (ln\ 2) \Big/ \frac{mv_0^2}{2kT} = \frac{(2\ ln\ 2).kT}{mc^2} . \lambda_0^2$$

or

$$\frac{b}{\lambda_0} = \frac{1}{c}\sqrt{\frac{(2\ ln\ 2)kT}{m}} = \frac{\sqrt{(2\ ln\ 2)\ R}}{c}\sqrt{\frac{T}{A}}, \quad . \quad . \quad . \quad (4)$$

where A = atomic weight.

The half-width is therefore greatest for the lighter elements. This is actually found to be the case. Hydrogen lines are always found to be very broad and diffuse. Lines due to very heavy elements like Cd and Hg are sharp. The temperature is also found to have marked effect. Michelson found that when tubes are immersed in liquid air, the spectral lines become remarkably sharp. But besides these qualitative proofs, the expression (4) can be subjected to a quantitative test. The breadth is generally very small. Yet that direct method *i.e.*, photographing a spectrum from a vacuum tube under different conditions, and then measuring the intensity of the line along its breadth by a micro-spectrophotometer (Koch, Moll or Zeiss pattern) has now been so improved that it has been found possible to obtain quantitative proof of (4). For this, original papers may be consulted. But a far more powerful method is to find out the limit of visibility of the line by a Fabry-Perot interferometer. This is an instrument of very great resolving power. It consists of plane parallel plates of glass which are half-silvered on the inside. If a beam of light is incident nearly normally, it suffers a large number of multiple reflections, and the interfering beams produce a series of sharp circular lines when observed by the eye. The different rings correspond to the different orders of interference, n, $n+1$, $n+2$... The maxima is very sharply defined, and the minima between two successive maxima has generally one-twentieth of the intensity of the maxima. But if the distance between the plates be gradually increased, this contrast diminishes, until at a critical distance the whole field of view is of uniform illumination. This limiting distance is found to be inversely proportional to the half-width b. It can be shown from the theory of the Fabry-Perot interferometer[1] that

$$\frac{\triangle}{\lambda} = C\sqrt{\frac{A}{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Fabry and Buisson took the value of C to be $1 \cdot 22 \times 10^6$ and verified the foregoing results experimentally. They used inert gases (He, Ne, Kr) to get line spectrum in the discharge tubes. The experiments were performed at two fixed temperatures (room and liquid air), the discharge tube being immersed in the latter case in a bath of liquid air. The following table summarises their results :—

Table 1.

Gas	Atomic Weight	Wave-length	Room Temp. $p = \triangle/\lambda$ (Obs.)	Room Temp. $p = \triangle/\lambda$ (Calc.)	Liquid Air Temp. p' obs.	p'/p
Helium	4	5876	144,000	144,000	241,000	1·66
Neon	20	5852	324,000	321,000	515,000	1·60
Krypton	83	5570	600,000	597,000	950,000	1·58

In the table p is put for $\triangle/\lambda$. It will be seen that the values of p (observed) and p (calculated) agree remarkably well.

NOTE 5

Deduction of Maxwell's Mean Free Path

On p. 158 we deduced for the mean free path the expression

$$\lambda = \frac{1}{n\pi\sigma^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

There we assumed that only one molecule moves with the velocity v while all the others are at rest. This is however only a hypothetical case; actually the molecules possess all possible velocities, the distribution of velocities among them being given by Maxwell's distribution law and this fact must be taken into account. Hence in traversing the distance v where v is the absolute velocity of a molecule, the molecule will collide with $\pi\sigma^2 rn$ other molecules, r being the mean relative velocity of the molecule with respect to the others. The mean free path of that moecule is therefore given by

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[1] Saha, *Phys. Rev.*, **10**, 782, 1917.

$$\lambda_v = \frac{1}{n\pi\sigma^2} \cdot \frac{v}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The molecule under consideration however may have all possible velocities in accordance with Maxwell's law. Therefore the mean free path averaged over molecules of all velocities is given by

$$\lambda = \frac{1}{n\pi\sigma^2} \; \frac{\bar{v}}{r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where v has been replaced by $\bar{v}$ the average velocity of the molecules, and r will now denote the mean relative velocity of *all* molecules with respect to all others. Following Clausius let us see how we can evaluate r.

Suppose that the particular molecule, whose relative velocity with respect to others we are finding, moves with the velocity c_1. Its relative velocity r_2 with respect to another molecule of velocity c_2 and making an angle θ with c_2 is

$$r_2 = (c_1{}^2 + c_2{}^2 - 2c_1c_2 \cos\,\theta)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now all the directions for the velocity c_2 are equally probable. Hence in order to find the average value of r_2 we must multiply r_2 by the probability that the velocity c_2 lies within the solid angle lying between θ and $\theta + d\theta$. Hence, as in equation 70, p. 168,

$$\begin{aligned} \bar{r}_2 &= \int_0^\pi \frac{r_2}{2} \sin\theta\, d\theta = \frac{1}{2}\int_0^\pi (c_1{}^2 + c_2{}^2 - 2c_1c_2 \cos\,\theta)^{\frac{1}{2}} \sin\theta\, d\theta \\ &= \frac{1}{6c_1c_2}\Big[(c_1{}^2 + c_2{}^2 - 2c_1c_2 \cos\theta)^{3/2}\Big]_0^\pi \quad . \quad . \quad . \quad . \quad . \quad (5) \end{aligned}$$

According to Clausius' assumption $c_1 = c_2 = v$. Therefore $r = \bar{r}_2 = 4v/3$ from (5). Equation (2) then yields for the mean free path of Clausius

$$\lambda = \frac{3}{4\pi n\sigma^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Let us further correct the expression by assuming Maxwell's law of distribution. We have to calculate r first by finding the relative velocity of a molecule having velocity c_1 with respect to molecules of velocity c_2 and averaging for all values of c_2 from 0 to ∞; next multiplying this mean value by the probability that the molecule has the velocity c_1 and averaging for values of c_1 from 0 to ∞. This procedure is adopted below :—

Equation (5) for the relative velocity $\bar{r}_2$ yields

$$\bar{r}_2 = \frac{1}{6c_1c_2}\Big[(c_1+c_2)^3 - (c_1\sim c_2)^3\Big] \quad . \quad . \quad . \quad (7)$$

It will be observed that we have written $(c_1\sim c_2)^3$ for $\{(c_1-c_2)^2\}^{3/2}$ instead of $(c_1-c_2)^3$. This is because the relative velocity r_2 given by (3) is always positive and therefore $(c_1^2+c_2^2-2c_1c_2\cos\theta)^{3/2}$ and $\{(c_1-c_2)^2\}^{3/2}$ must also be always positive whatever the values of c_1 and c_2. Hence when $c_1>c_2$ we must use $(c_1\sim c_2)^3=(c_1-c_2)^3$ and when $c_1<c_2$ we should use $(c_1\sim c_2)^3=(c_2-c_1)^3$. Therefore

for $c_1>c_2$,
$$\bar{r}_2 = \frac{3c_1^2+c_2^2}{3c_1}, \quad . \quad . \quad . \quad . \quad (7a)$$

and for $c_1<c_2$,
$$\bar{r}_2 = \frac{3c_2^2+c_1^2}{3c_2}. \quad . \quad . \quad . \quad . \quad (7b)$$

The probability that there exist molecules of the velocity c_2 is

$$4\pi a^3 e^{-bc_2^2}\, c_2^2\, dc_2.$$

Hence the average relative velocity of the molecule c_1 with respect to all others is

$$r_1 = \int_0^\infty \bar{r}_2 .\, 4\pi a^3 e^{-bc_2^2}\, c_2^2\, dc_2. \quad . \quad . \quad . \quad (8)$$

Since $\bar{r}_2$ has two different values depending upon whether c_1 is greater than c_2 or not, we should rewrite (8) as

$$r_1 = \int_0^{c_1} \frac{3c_1^2+c_2^2}{3c_1}\, 4\pi a^3 e^{-bc_2^2}\, c_2^2 dc_2 + \int_{c_1}^{\infty} \frac{3c_2^2+c_1^2}{3c_2}\, 4\pi a^3 e^{-bc_2^2}\, c_2^2\, dc_2 \quad . \quad (9)$$

We must multiply this value of r_1 by the probability of existence of molecules having the velocity c_1, which is $4\pi a^3 e^{-bc_1^2}\, c_1^2 dc_1$. Thus the average velocity r of any molecule with respect to all others in space is

$$\begin{aligned} r = \bar{r}_1 = & \int_0^\infty 4\pi a^3 e^{-bc_1^2}\, c_1^2\, dc_1 \int_0^{c_1} \frac{3c_1^2+c_2^2}{3c_1}\, 4\pi a^3 e^{-bc_2^2}\, c_2^2\, dc_2 \\ & + \int_0^\infty 4\pi a^3 e^{-bc_1^2}\, c_1^2 dc_1 \int_{c_1}^\infty \frac{3c_2^2+c_1^2}{3c_2} .\, 4\pi a^3 e^{-bc_2^2}\, c_2^2\, dc_2 \\ & = 16\pi^2 a^6 (I_1+I_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10) \end{aligned}$$

where

$$I_1 = \int_0^\infty c_1^2 e^{-bc_1^2} dc_1 \int_0^{c_1} \frac{3c_1^2+c_2^2}{3c_1} c_2^2 e^{-bc_2^2} dc_2$$

$$I_2 = \int_0^\infty c_1^2 e^{-bc_1^2} dc_1 \int_{c_1}^\infty \frac{3c_2^2+c_1^2}{3c_2} c_2^2 e^{-bc_2^2} dc_2$$

The integral I_2 can be readily evaluated. In the expression for I_1 the order of integration may be reversed, the integration being performed first with respect to c_1 and the limits of integration correspondingly altered. It will be seen[1] that I_1 is of the same form as I_2 and

$$I_1 = I_2 = \frac{1}{8\sqrt{2}}\left(\frac{\pi}{b^7}\right)^{\frac{1}{2}}.$$

Hence
$$r = \frac{4}{\sqrt{2b\pi}} = 4\sqrt{\frac{kT}{m\pi}} = \bar{c}\sqrt{2}. \qquad (11)$$

Hence from (3) we get[2] for the mean free path of Maxwell

$$\lambda = \frac{1}{\sqrt{2}\, n\pi\sigma^2}. \qquad (12)$$

The method can be adopted to calculate the mean free path of one type of gas in a mixture of gases. We have to utilise (9) to find r with the condition that a and b are different for the two types. For details of calculation see Kennard, *Kinetic Theory of Gases* (1938), pp. 108-112.

NOTE 6

Determination of Avogadro Number and the Size of Molecules

Historically the kinetic theory of gases was the first to give an idea of the molecular magnitudes. The method was given by Loschmidt in 1865 and was improved by Sutherland in 1893. The method is however not capable of any great accuracy, partly because of the fact that the formulae employed are not quite rigorous and partly because they involve the assumption that the molecule is a structureless spherical body. This assumption cannot be justified in the light of modern theories of structure of matter. More accurate methods were developed later so that the methods based on the kinetic theory are now only of historical interest; still, however, they give us qualitative results and are important since they are deduced directly from the dynamics of a system of molecules. We shall first give the kinetic theory methods.

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[1] For details see Bloch, *Kinetic Theory of Gases*, p. 171.

[2] This result can also be obtained in a different way due to Maxwell. For details see Jeans, *Kinetic Theory of Gases* (1940), pp. 131-135.

A. KINETIC THEORY METHODS

In the text we have already deduced expressions for the viscosity, conduction of heat and diffusion in terms of the mean free path. Consider first the viscosity η (p. 169). It is shown there that

$$\eta = \tfrac{1}{3}\rho\bar{c}\lambda.$$

Now $$\bar{c} = \sqrt{\frac{8kT}{m\pi}}, \qquad \lambda = \frac{1}{\sqrt{2}\,n\pi\sigma^2} = \frac{V}{\sqrt{2}\,N\pi\sigma^2},$$

where n is the molecular density, N the Avogadro number and V the gram-molecular volume. Hence

$$\eta = \frac{V}{3\sqrt{2}}\,\frac{mn}{N\pi\sigma^2}\sqrt{\frac{8kT}{m\pi}} = \frac{2}{3\pi^{3/2}}\cdot\frac{1}{N\sigma^2}\sqrt{MRT}. \qquad (1)$$

Thus $N\sigma^2$ can be evaluated from a simple measurement of the coefficient of viscosity η. M = molecular weight.

Next by a study of the deviation of gases from Boyle's law we can determine the value of b which is four times the gram-molecular volume *i.e.*

$$b = \frac{2}{3}N\pi\sigma^3 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This gives the product $N\sigma^3$. Knowing the value of $N\sigma^2$ and $N\sigma^3$ from (1) and (2) respectively, both the quantities N and σ may be determined. We have

$$N = \frac{32}{243}\cdot\frac{(MRT)^{3/2}}{b^2\eta^3\pi^{5/2}}, \qquad \sigma = \frac{9\eta b}{4}\sqrt{\frac{\pi}{MRT}}. \quad . \quad . \quad (3)$$

By simple substitution it can be easily seen that $N = 6\times10^{23}$ and σ is of the order of 10^{-8} cm. In place of viscosity we can as well employ the expressions for the conduction of heat or the coefficient of diffusion. We have thus three methods of determining N from the kinetic theory alone.

If however we assume N to be known from electrical or other phenomena, equations (1) and (2) furnish two independent methods of determining σ. Table[1] 1 gives the value of σ obtained by these methods.

It will be seen that the values of $\frac{1}{2}\sigma$ obtained from the mean free path phenomena and from the value of 'b' do not agree well. This is

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[1] Taken from Jeans, *Dynamical Theory of Gases*, 4th Edition, p. 329.

Table 1.—*Values of molecular radius by different methods.*

Gas	Values of $\frac{1}{2}\sigma\times10^8$ calculated from			
	Viscosity	Conduction of heat	Diffusion	Value of *b*
Hydrogen ..	1·36 cm.	1·36 cm.	1·36 cm.	1·27 cm.
Helium ..	1·09	1·10	..	0·99
Nitrogen ..	1·89	1·89	1·92	1·78
Air	1·87	1·87	1·87	1·66
Carbon dioxide..	2·31	2·42	2·19	1·71
Oxygen ..	1·81	1·81	1·82	1·45

because the molecules are not hard elastic spheres as assumed in the elementary kinetic theory. We know from recent developments in Physics that the atoms consist of electrons and a positive nucleus. Such a structure is penetrable as experiments on the scattering of α-particles actually show. Hence the molecules cannot be treated as hard elastic spheres and the force exerted during a so-called "collision" must be wholly electrical. From these considerations it will be seen that the average minimum distance between the nuclei of two molecules during collisions is regarded as the molecular diameter and would correspond to the diameter σ of hard molecules.

The elementary kinetic theory has been improved by taking into account this softness of the molecule. Hydrogen and helium are the hardest molecules. Detailed considerations,[1] which can only be referred to here, show that for these gases there is a correcting factor 1·079 by which we must divide the value of $\frac{1}{2}\sigma$ obtained from Van der Waals' law.

After making the above correction and certain others, it will be seen that the values of $\frac{1}{2}\sigma$ obtained from values of *b* are systematically smaller than those obtained from the mean free path phenomena. A very simple geometrical consideration shows that this would be the case if the molecules have some shape other than the spherical. For, in measuring deviations from Boyle's law we are concerned with the volume of the molecule and in the mean free path phenomena we are concerned with the cross-section of the molecule. And the mean radius of the molecule regarded as a rigid sphere will be less than the mean radius of the cross-section if the molecule is not spherical.

To make the point clearer we take a specific case. Suppose the molecules consist of coin-shaped discs of radius r and small thickness h.

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[1] See Jeans, *Dynamical Theory of Gases*, Chapters XI and XIV.

The deviations from Boyle's law will give the values of σ given by $(\frac{4}{3})\pi(\sigma/2)^3 = \pi r^2 h$, or $\sigma = (6r^2h)^{1/3}$, while the mean free path phenomena would give the value $\sigma = r$. If h is very small, it is obvious that $(6r^2h)^{1/3} < r$.

Equations (1) and (2) clearly show that the problems of finding N and σ are identical, since if one has been determined the other can be known by any one of these equations. Hence any method for finding N may as well be called a method for finding σ and *vice versa.*

Various methods for determining the Avogadro number from measurements of the Brownian Movement have already been given in the text (pp. 185—196).

B. METHODS BASED ON BLACK-BODY RADIATION

On p. 673 it is proved that the Wien constant b is given by the relation

$$b = \frac{ch}{4\cdot 9651k}, \qquad \ldots \ldots \qquad (4)$$

where h is the Planck constant and k the Boltzmann constant. Now b can be determined experimentally (p. 662) and h obtained from Millikan's photoelectric experiments or otherwise. Hence k can be calculated from (4), and from the relation $R = Nk$, the value of Avogadro number N can be easily obtained. Thus we have $b = \cdot 2884$ cm. × degrees, $h = 6\cdot 55 \times 10^{-27}$, $R = 8\cdot 313 \times 10^7$; whence $N = 60\cdot 59 \times 10^{22}$.

Again on p. 672, we have proved that the Stefan's constant

$$\sigma = \frac{2\pi^5 k^4}{15c^2h^3}. \qquad \ldots \ldots \qquad (5)$$

Now σ can be determined experimentally (§§ 15·23 and 15·24) and, substituting the value of h in (6) we can get k and hence N. Thus experimentally we have $\sigma = 5\cdot 77 \times 10^{-5}$ ergs/cm, from which, with the aid of (5), we obtain $N = 60\cdot 39 \times 10^{22}$.

We can however obtain N from the theory of radiation alone, for we can eliminate h from (4) and (5) and obtain an expression for k. In this way we get $N = 60\cdot 12 \times 10^{22}$.

But the radiation constants are not known very accurately, hence the best value of N is obtained from indirect methods. These are outside the subject of heat and hence we shall indicate them only briefly in this place.

C. METHODS BASED ON THE DETERMINATION OF ELECTRONIC CHARGE

We know from the theory of electrolytes that

$$F = Ne, \qquad \ldots \ldots \qquad (6)$$

where F is the charge carried by a gram-equivalent of a monovalent ion and is equal to 96540 coulombs. The electronic charge e can be found directly as by Millikan or indirectly by determining the charge on the α-particle which is equal to $2e$ (Regener). Using the value $e = 4 \cdot 801 \times 10^{-10}$ e. s. u. we get $N = 60 \cdot 1 \times 10^{22}$.

D. FROM MEASUREMENTS OF DIELECTRIC CONSTANT

Considering the molecules as spherical conductors of electricity, Clausius and Mossotti obtained for a gas the relation

$$\mathscr{K} - 1 = \tfrac{4}{3} n\pi\sigma^3 \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $\mathscr{K}$ is the dielectric constant of the gas and n the number of molecules per c.c. Knowing $\mathscr{K}$ and σ, n can be calculated. If $\mathscr{K}$ is not known, we can determine $\mathscr{K}$ from Maxwell's relation $\mathscr{K} = \mu^2$ where μ is the refractive index of the gas.

We give below a summary of the important methods* by means of which the Avogadro number can be determined.

Table 2.—The Avogadro number N, by various methods.

No.	Method	Method first given by	$N \times 10^{-22}$	Calculation of N depends upon measurements of
1.	Kinetic Theory of Gases (viscosity, heat conduction, etc.).	Loschmidt (1865) corrected by Sutherland (1893).	59·5 to 68	Eucken, *Phys. Zeits.* **14**, 324, 1913.
2.	Brownian movement			
	(*a*) Vertical distribution of particles.	Perrin (1909).	60·9	Perrin, *The Atoms.*
	(*b*) Change of position of particles.	Einstein (1905).	59·1	Nordlund, *Zeits. f. Phys. Chem.*, **87**, 40.
			60·3	Fletscher, *Phys. Rev.* **4**, 440, 1914.
			60·4	Eyring, *Phys. Rev.* **5**, 412, 1915.
3.	Surface Tension of very dilute sodium oleate solution.	De Noüy (1924).	60·0	De Noüy, *Phil. Mag.*, **48**, 664, 1924.

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* Virgo (*Science Progress*, **108**, 634, 1933) has enumerated more than eighty different experimental determinations of this quantity made upto 1933. For an excellent summary of the different methods, see Loeb, *Kinetic Theory of Gases*, (1934), pp. 408-423

No.	Method	Method first given by	$N \times 10^{-22}$	Calculation of N depends upon measurements of
4.	Law of Black-body Radiation.	Planck (1900).	60·5	Gerlach, *Zeits. f. Physik*, **2**, 76, 1920. Warburg and Müller, *Ann. d. Physik*. **48**, 410, 1917.
5.	Determination of the charge			
	(*a*) on the electron (Oil drops).	Townsend (1897) improved by Millikan (1910).	60·62	Millikan *Phil. Mag.* **34**, 1, 1917.
	(*b*) on α-particles.	Regener (1908).	60·4	Regener, *Berl. Akad.* 1909, p. 948.
6.	Scattering of light by Earth's atmosphere.	Lord Rayleigh (1899).	60·4	Fowle, *Astrophys. Jour.*, **40**, 435, 1914.
7.	Fine Structure of Hydrogen lines.	Sommerfeld (1916).	60·8	Paschen, *Ann. d. Physik*, **50**, 901, 1906.
8.	Magnitude of elementary cube of a crystal obtained with X-rays.	A. Compton (1922).	60·35	Bäcklin. *Diss.* Upsala (1928).

NOTE 7

Stirling's Formula

The value of the quantity $N\,!$ very rapidly increases with n. In fact, $30\,!$ gives us a number which requires 33 figures to write, and $400\,!$ requires 869 figures. An approximate formula for finding out the value of $n\,!$ was given by Stirling. This is

$$n\,! = \frac{n^n}{e^n}\sqrt{2\pi n}\left(1 + \frac{1}{12n} + \frac{1}{228n^2} - \frac{139}{51840\,n^3} + \cdots\cdots\right).$$

For the purpose of this book, it will suffice to use the less approximate formula

$$ln\ n! = n\,(ln\ n-1).$$

This can be proved as follows :--

$$ln\ n! = ln\,1+ ln\,2+ln\,3+.\ \ .\,ln\,x+.\ \ .\,ln\ n.$$

$$ln\ n^n = ln\ n+ln\ n+\ .\ .\ .\ .\ .\ .\ ln\ n+.\ \ .\,ln\ n.$$

Hence $ln\left(\frac{n!}{n^n}\right) = ln\frac{1}{n}+ln\frac{2}{n}+\dots ln\frac{x}{n}+.\ \ .\,ln\frac{n}{n}$

$$=\Sigma\,(ln\ x-ln\ n).$$

The summation can be replaced, though not quite rigorously, by the integration

$$\int_1^n (ln\ x-ln\ n)\,dx = \Big[x\,ln\,x-x\Big]_1^n-\Big[x\,ln\,n\Big]_1^n = -(n-1)+ln\ n.$$

Hence $\qquad ln\ n! = n\,(ln\ n-1)+ln\ n+1,$

and the last two terms may be neglected in comparison with others when n is very large.

NOTE 8

Proof of Liouville's Theorem.

Let $q_1, q_2 \dots q_n$ and $p_1, p_2 \dots p_n$ denote the position and momentum coordinates. Then according to this theorem

$$\frac{d}{dt}\,(\Pi\,\triangle p\cdot\triangle q) = 0,$$

i.e., any arbitrary element of volume in phase space does not change its size with time. To prove this, let us put,

$$\triangle\tau = \triangle p_1\cdot\triangle p_2\dots\triangle p_n\cdot\triangle q_1\cdot\triangle q_2\dots\triangle q_n$$

If $\triangle\tau$ is the volume of the element after a small interval of time dt, then

$$\triangle\tau' = \triangle(p_1+\dot p_1dt)\cdot\triangle(p_2+\dot p_2dt)\dots\triangle(p_n+\dot p_ndt)\cdot\triangle(q_1+\dot q_1dt)\cdot\triangle(q_n+\dot q_ndt)\cdot$$

Since $\quad \triangle\dot p_1 = \frac{\partial\dot p_1}{\partial p_1}\triangle p_1\dots$ etc. $\quad \triangle\dot q_1 = \frac{\partial\dot q_1}{\partial q_1}\triangle q_1\dots$ etc.

we have

$$\triangle\tau' = \triangle p_1\cdot\triangle p_2\dots\triangle p_n\cdot\triangle q_1\cdot\triangle q_2\dots\triangle q_n\left(1+\frac{\partial\dot p_1}{\partial p_1}dt\right)\times$$

$$\left(1+\frac{\partial\dot p_2}{\partial p_2}dt\right)\dots\left(1+\frac{\partial\dot p_n}{\partial p_n}dt\right)\left(1+\frac{\partial\dot q_1}{\partial q_1}dt\right)\dots\left(1+\frac{\partial\dot q_n}{\partial q_n}dt\right)$$

$$\text{Or } \triangle\tau' = \triangle\tau\left[1+\left(\frac{\partial \dot p_1}{\partial p_1}+\frac{\partial \dot p_2}{\partial p_2}+\dots+\frac{\partial \dot p_n}{\partial p_n}+\frac{\partial \dot q_1}{\partial q_1}+\dots+\frac{\partial \dot q_n}{\partial q_n}\right)dt\right].$$

$$\therefore \triangle\tau' - \triangle\tau = \triangle\tau\left(\frac{\partial \dot p_1}{\partial p_1}+\frac{\partial \dot p_2}{\partial p_2}+\dots+\frac{\partial \dot p_n}{\partial p_n}+\frac{\partial \dot q_1}{\partial q_1}+\dots+\frac{\partial \dot q_n}{\partial q_n}\right)dt.$$

Since, however,

$$\dot p_r = -\frac{\partial H}{\partial q_r} \text{ and } \dot q_r = \frac{\partial H}{\partial p_r}$$

where H is the Hamiltonian function of the system, the right-hand side identically vanishes. Hence $\triangle\tau$ does not change with time, *i.e.*,

$$\frac{d}{dt}(\Pi\triangle p.\ \triangle q) = 0.$$

We have now to show that the elementary volume $\triangle\tau$ is independent of the choice of the system of coordinates. Let ϕ be the position and ψ the corresponding momentum coordinates in another system of coordinates. We have then to show that

$$\triangle\tau_q = \triangle\tau_\phi.$$

Evidently ϕ's and ψ's must be some functions of q's and p's. Let us now choose another set of position and momentum coordinates $(x_1, x_2, \dots x_n)$ and $(y_1, y_2, \dots y_n)$ respectively which are also functions of the original coordinates. Let us further suppose that these coincide with q's and p's at a certain time t and with ϕ's and ψ's at another time t'. Then

$$\triangle\tau_x = \triangle\tau_q \text{ and } \triangle\tau_x{}' = \triangle\tau_\phi{}',$$

where $\triangle\tau$ and $\triangle\tau'$ denote the volumes at t and t'. Since, however, as proved above

$$\triangle\tau_x = \triangle\tau_x{}',$$

We have
$$\triangle\tau_q = \triangle\tau_\phi{}' = \triangle\tau_\psi.$$

The element of phase volume is thus independent of the choice of coordinates.

NOTE 9

Proof of Boltzmann's Theorem $S = k \log W$

We have on p. 388 the functional equation

$$f(W_1W_2) = f(W_1) + f(W_2), \quad . \quad . \quad . \quad . \quad (1)$$

the solution of which determines f. To solve this let us differentiate (1) with respect to W_1, keeping W_2 constant. We get

$$W_2\, \dot f(W_1W_2) = \dot f(W_1).$$

Similarly $$W_1\,\dot{f}(W_1W_2) = \dot{f}(W_2)$$

Hence $$W_1\,\dot{f}(W_1) = W_2\,\dot{f}(W_2) = W_1W_2\,\dot{f}(W_1W_2),$$

or $$W_1\,\dot{f}(W_1) = W_2\,\dot{f}(W_2) = \text{const.}$$

$$\therefore \qquad f(W) = k\log W + C.$$

The constant k is a universal constant, being the same for all systems but C is not necessarily the same for all systems.

NOTE 10

Energy of Oscillators in a Field of Radiation

Let us consider a number of linear simple harmonic oscillators of all frequencies in equilibrium with radiation and let us find the average energy of the oscillators in terms of the density of radiation. For solving this problem, Planck considered the absorption and emission from these oscillators separately. The energy absorbed by an oscillator of charge e and mass m from the field of radiation of density u_ν is $\frac{\pi e^2}{3m}u_\nu\,dt$, whereas the emission, when the oscillator has the energy E is $E\,\frac{2e^2(2\pi\nu)^2}{3mc^3}\,dt$. For equilibrium, the time average of these quantities must be equal. Hence

$$u_\nu = \frac{8\pi\nu^2}{c^3}\,\bar{E}.$$

We shall however deduce this result from the equation of motion of an oscillator as this method is shorter.

Let us suppose that a linear simple harmonic oscillator, consisting of an electron, is placed in the field of radiation. The equation of motion of the electron is given by

$$m\ddot{x}+\mu x = F, \qquad \ldots\ldots \qquad (1)$$

where F is the impressed external field due to radiation, and the oscillator is not subjected to any damping. But this last assumption is not true, as according to classical electrodynamics, the oscillator radiates at any instant the amount of energy $S=\frac{2}{3}\frac{e^2}{c^3}\ddot{x}^2\,\frac{\text{erg}}{\text{sec.}}$, but the energy of a simple harmonic oscillator is constant and it cannot radiate energy. To F, we must therefore add some damping force. Let it be denoted by F'. Putting $F=0$, we can obtain F' by equating the average work done *against* it by the oscillators to $\bar{S}$, the average radiation of energy, *i.e.*, from the condition

$$\frac{1}{T}\int_0^T F'\dot{x}\,dt = -\bar{S} = -\frac{2}{3T}\frac{e^2}{c^3}\int_0^T \ddot{x}^2\,dt.$$

Since $\frac{d}{dt}\left(\dot{x}\,\ddot{x}\right) = \ddot{x}^2 + \dot{x}\,\dddot{x}$, we have

$$\int_0^T \ddot{x}^2 dt = \int_0^T \frac{d}{dt}\left(\dot{x}\,\ddot{x}\right)dt - \int_0^T\left(\dot{x}\,\dddot{x}\right)dt = \left[\dot{x}\,\ddot{x}\right]_0^T - \int_0^T\left(\dot{x}\,\dddot{x}\right)dt.$$

$$\therefore \frac{1}{T}\int_0^T\left(F'\dot{x}\right)dt = -\frac{2}{3}\frac{e^2}{c^3T}\left[\dot{x}\,\ddot{x}\right]_0^T + \frac{2}{3}\frac{e^2}{c^3T}\int_0^T \dot{x}\,\dddot{x}\,dt.$$

The first term on the right side is zero, if T be sufficiently large, which is always allowed. Hence we must have

$$\frac{1}{T}\int_0^T\left(F'\dot{x}\right)dt = \frac{2}{3}\frac{e^2}{c^3T}\int_0^T \dot{x}\,\dddot{x}\,dt$$

This is satisfied if

$$F' = \frac{2}{3}\frac{e^2}{c^3}\dddot{x}. \qquad (2)$$

This force is known as "*Radiation Damping*". The equation of motion is now given by

$$m\ddot{x} + \mu x - \frac{2}{3}\frac{e^2}{c^3}\dddot{x} = F. \qquad (3)$$

When $F = 0$, we obtain free motion of the oscillator. It can be shown easily that the free motion is given by

$$x = e^{-\gamma t/2}\left(a_0\cos\omega_0 t + b_0\sin\omega_0 t\right) \qquad (4)$$

where $\omega_0^2 = \mu/m,\ \gamma = \frac{2}{3}\cdot\frac{e^2}{mc^3}\omega_0^2.$

This is the equation of a damped oscillator.

When the oscillator is moving in a radiation field, we can put $F = eE_x$ where E_x is the electrical intensity of radiation and is given by

$$E_x = \frac{1}{2}\sum_{-\infty}^{\infty} a_n\, e^{inat} \qquad (5)$$

and e is the charge on the electron and $a/2\pi$ is some fundamental frequency. Since the radiation is continuous, it has been decomposed into a Fourier series. To have E_x real, we must have

$$a_{-n} = a_n^*. \qquad (6)$$

where a_n^* denotes the conjugate complex of a_n. According to Maxwell's Theorem, the energy density u of radiation in space is given by

$$u = \frac{1}{8\pi}\left[\overline{E_x^2} + \overline{E_y^2} + \overline{E_z^2} + \overline{H_x^2} + \overline{H_y^2} + \overline{H_z^2}\right] = \frac{3}{4\pi}\overline{E_x^2}. \qquad (7)$$

since for isotropic radiation all these mean square quantities are equal.

But $$E_x^2 = \frac{1}{4}\sum a_n\, a_{-n}\, e^{i(n-n')at}$$

Thus the time average becomes zero unless $n=n'$, and we have

$$\overline{E_x^2} = \frac{1}{2}\sum_{n=0}^{n=\infty} |a_n|^2 \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and therefore

$$u = \frac{3}{8\pi}\sum_{n=0}^{\infty} |a_n|^2 . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The incident energy lying between ν and $\nu+d\nu$ is given by the relation

$$u_\nu\, d\nu = \frac{3}{8\pi}\,\overline{|a_n|}^2\,\frac{2\pi}{a}\,d\nu \quad . \quad . \quad . \quad . \quad . \quad (10)$$

since $$n = 2\pi\nu/a. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Hence $$u_\nu = \frac{3}{4a}\,\overline{|a_n|}^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Now the integration of (3) with E_x as given by (5) can be easily performed by ordinary known methods. We expand the function $x(t)$ in the form

$$x = \frac{1}{2}\sum_{n=-\infty}^{n=+\infty} \xi_n\, e^{inat} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Substituting the values of x and E_x from (13) and (5) respectively in equation (3) we obtain for the amplitude ξ_n the equation

$$\xi_n\left[-(na)^2+\omega_0^2+i\,\frac{2e^2}{3mc^3}\,(na)^3\right] = \frac{e}{m}\,a_n.$$

From this we get

$$\xi_n^*\xi_n = |\xi_n|^2 = \frac{\dfrac{e^2}{m^2}\,|a_n|^2}{\left\{(na)^2-\omega_0^2\right\}^2 + \left\{\dfrac{\frac{2}{3}\,e^2(na)^3}{mc^3}\right\}^2} \quad . \quad . \quad (14)$$

We now find the energy E of the oscillator. Since this is equal to double the average kinetic energy we have

$$\overline{E} = \overline{m\dot{x}^2} = \frac{m}{4}\overline{\left\{\sum_{-\infty}^{+\infty} ina\xi_n e^{inat}\right\}^2} \quad . \quad . \quad . \quad . \quad (15)$$

Calculating as before in the case of $\overline{E_x^2}$ we have the time average

$$\overline{E} = \frac{m}{2}\sum_{n=0}^{\infty}(na)^2\,|\xi_n|^2. \quad . \quad . \quad . \quad . \quad . \quad (16)$$

since in place of a_n in (5) we have now $i\xi_n.na$.

Substituting the value of $|\xi_n|^2$ from (14) and replacing the summation by integration, remembering that $\omega = na$, or $dn = \frac{d\omega}{a}$ we obtain

$$\overline{E} = \frac{m}{2}\frac{e^2}{m^2}\int_0^{\infty}\frac{\omega^2}{\left\{\omega^2-\omega_0^2\right\}^2+\left\{\frac{2}{3}\frac{e^2\omega^3}{mc^3}\right\}^2}\,|a_n|^2\,\frac{d\omega}{a}$$

This integrand has sharp maximum at $\omega = \omega_0$. We can therefore replace ω by ω_0 everywhere, excepting where $\omega - \omega_0$ occurs, and take the limits of integration from $-\infty$ to $+\infty$. Further we introduce the integration variable $\omega - \omega_0 = x$. Thus we have

$$\overline{E} = \frac{e^2}{2m}\frac{\overline{|a_n|^2}}{a}\,\omega_0^2\int_{-\infty}^{+\infty}\frac{dx}{4\omega_0^2x^2+\left(\frac{2}{3}\frac{e^2\omega_0^3}{mc^3}\right)^2}, \quad . \quad . \quad . \quad (17)$$

where $\overline{|a_n|^2}$ is the value of $|a_n|^2$ at $na = \omega_0$.

Putting $\frac{3mc^3x}{e^2\omega_0^2} = z$, equation (17) reduces to

$$\overline{E} = \frac{e^2}{2m}\frac{\overline{|a_n|^2}}{a}\,\omega_0^2\,\frac{3mc^3}{4e^2\omega_0^4}\int_{-\infty}^{+\infty}\frac{dz}{z^2+1} = \frac{c^3}{2\omega_0^2}\,\pi u_\nu$$

since the integral is equal to π and from (12), $\frac{\overline{|a_n|^2}}{a} = \frac{3}{4}u_\nu$.

Hence finally we get since $\omega_0 = 2\pi\nu$,

$$u_\nu = \frac{8\pi\nu^2}{c^3}\,\overline{E} \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

NOTE[1] 11

Nuclear Spin from Molecular Spectra

It was first observed by Mecke that the band lines due to the spectrum of diatomic molecules show a remarkable alternation of intensity. In the case of molecules like He_2 and O_2 the alternate lines are entirely absent, while in the case of H_2, the alternate lines have the intensity 3 : 1. Similar alternations are found in the case of all diatomic molecules where the two nuclei are identical. Heisenberg was the first to observe that the case was analogous to that of the spectrum of the He-atom, whose lines can be grouped into two sets—the parhelium lines and the orthohelium lines. The parhelium lines arise from a singlet set of terms, and the orthohelium lines from a triplet set, and terms of the one set do not usually combine with those of the other. (For a description of the case, see Saha and Saha, *Treatise on Modern Physics*, p. 557, and for explanation from wave mechanics, see Sommerfeld, *Wave-Mechanical Supplement*, p. 267). The explanation of the occurrence of this phenomenon is that when the electrons are interchanged, the eigenfunctions of the different states should change their sign, *i.e.*, should be anti-symmetrical. The interchange includes spin, as well as space coordinates.

In the case of molecules composed of two identical atoms, the rotational eigenfunction (due to rotation of the molecule about a line passing through the C. G. and perpendicular to the nuclear axis) is given by $e^{is\phi}$, where $s = 0, 1, 2. \ldots .$ any integral number. If we now interchange the nuclei, the process is equivalent to substituting $\pi+\phi$ for ϕ, and it is easy to see that $e^{is\phi}$ remains the same if s is an even number, but changes its sign when s is odd. Hence the rotational terms corresponding to $s = 0, 2, 4. . .$ are symmetrical in the two nuclei, but those corresponding to $s = 1, 3, 5, . .$ are anti-symmetrical.

Let us now suppose that each of the two nuclei possesses the spin-moment 'i'. Then each nucleus is capable of taking $2i+1$ positions, corresponding to the m_i-values $i, i-1, i-2, \ldots -i$. Here m signifies cos θ, where θ is the angle between the nuclear axis and a fixed direction in space. When we take two nuclei a and b, any one of the $(2i+1)$ orientations of a can combine with any of the $(2i+1)$ orientations of b, so the total number of combinations is $(2i+1)^2$. But let us put the further restriction that the combinations are either to be symmetrical or anti-symmetrical. All the $(2i+1)^2$ combinations can be represented by the terms x_{jl} of the square matrix $[x_{jl}]$ where $j = i, i-1, \ldots -i$, and x_{jl} denotes a combination in which 'a' has the m_i-value j, and b has the value l. Now if the combination is symmetrical in a, b, we should have $x_{jl}=x_{lj}$, *i.e.* the, sign is not changed by interchanging j and l. It can be easily seen that the number of combinations in this case is $(i+1)(2i+1)$. But if the combination is anti-symmetrical, we have $x_{jl}=-x_{lj}$. Now the diagonal terms $x_{jj}=-x_{jj}=0$, hence the number of independent terms is $i(2i+1)$. We thus find

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[1] This note should be read after note 15.

$g_{ks}=(i+1)(2i+1)$ for symmetrical combination of nuclear spin.
$g_{ka}=i(2i+1)$ for anti-symmetrical combination of nuclear spin.

Now let us consider the combined symmetry. We represent by

ψ_{rs} . . . the symmetrical eigenfunction for rotation.
ψ_{ra} . . . anti-symmetrical ,, ,, ,,
ψ_{ks} . . . symmetrical eigenfunction for nuclear spin
ψ_{ka} . . . anti-symmetrical ,, ,, ,,

Then remembering that the ultimate ψ-functions will be either symmetrical or anti-symmetrical, we have the following cases :—

I. Symmetrical	II. Anti-symmetrical
A. $\psi_{rs}\cdot\psi_{ks}$ $s=0, 2, 4, \ldots\ g_{ks}=(i+1)(2i+1)$	A. $\psi_{rs}\cdot\psi_{ka}$ $s=0, 2, 4, \ldots\ g_{ka}=i(2i+1)$
B. $\psi_{ra}\cdot\psi_{ka}$ $s=1, 3, 5 \ldots\ g_{ka}=i(2i+1)$	B. $\psi_{ra}\cdot\psi_{ks}$ $s=1, 3, 5, \ldots\ g_{ka}=(i+1)(2i+1)$

This explains the result given in §§ 16·9 and 16·10. We have for the hydrogen molecule, the B-terms ($s=1,3,5\ldots$) thrice as numerous as A-terms. Hence

$$\frac{g_{ks}}{g_{ka}}=\frac{i+1}{i}=3, \quad \text{or } i=\frac{1}{2},$$

i.e., the H-atom has the nuclear spin $\frac{1}{2}$, and the molecule obeys FD-statistics. But for nitrogen, it was found by Ornstein and Van Eyck that for N_2^+-bands, the A-terms ($s=0, 2, 4,$) are twice as numerous as B-terms ($s=1, 3, 5\ldots$). This cannot happen if the molecule is of type II., *i.e.*, if it obeys FD-statistics. We therefore suppose that the N_2-molecule is of type I., *i.e.*, obeys BE-statistics, and

$$\frac{g_{ks}}{g_{ka}}=\frac{i+1}{i}=2, \quad \text{hence } i=1.$$

We observe that when $i=0$ (case of He_2, C_2, $O_2\ldots$), only one set of terms is present—A-terms when the molecule obeys BE-statistics, B-terms when it obeys FD-statistics. (*vide*, Krönig, *Phys. Zeits.* **32**, 774, 1931).

NOTE 12

Table 1.—C_v after Einstein for $h\nu/kT$ from 0 to 14.

$h\nu/kT$	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
0	5·955	5·947	5·935	5·911	5·878	5·833	5·780	5·718	5·648	5·568	5·483
1	5·483	5·401	5·279	5·184	5·071	4·954	4·832	4·706	4·578	4·446	4·312
2	4·312	4·176	4·039	3·902	3·764	3·626	3·489	3·353	3·218	3·086	2·954
3	2·954	2·827	2·701	2·578	2·458	2·342	2·229	2·119	2·013	1·910	1·811
4	1·811	1·715	1·623	1·536	1·451	1·370	1·292	1·218	1·148	1·081	1·017
5	1·017	0·956	0·898	0·843	0·791	0·743	0·696	0·652	0·610	0·571	0·535
6	0·535	0·499	0·466	0·436	0·407	0·379	0·354	0·330	0·307	0·286	0·266
7	0·266	0·248	0·231	0·215	0·200	0·185	0·172	0·160	0·149	0·138	0·128
8	0·128	0·119	0·110	0·102	0·0945	0·0884	0·0811	0·0752	0·0695	0·0650	0·0600
9	0·0600	0·0554	0·0509	0·0468	0·0435	0·0400	0·0372	0·0340	0·0310	0·0286	0·0266
10	0·0266	0·0247	0·0231	0·0212	0·0196	0·0180	0·0167	0·0152	0·0142	0·0129	0·0119
11	0·0119	0·0110	0·0102	0·0093	0·0085	0·0078	0·0073	0·0067	0·0062	0·0057	0·0052
12	0·0052	0·0048	0·0045	0·0041	0·0038	0·0035	0·0032	0·0029	0·0027	0·0024	0·0022
13	0·0022	0·0020	0·0019	0·0017	0·0016	0·0015	0·0014	0·0013	0·0012	0·0011	0·0010

Table 2.—C_v after Debye for $\frac{\Theta}{T}$ from 0 to 30

$\frac{\Theta}{T}$	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
0	5·955	5·95	5·94	5·93	5·91	5·88	5·85	5·81	5·77	5·72	5·67
1	5·670	5·61	5·55	5·48	5·41	5·34	5·26	5·18	5·09	5·01	4·92
2	4·918	4·83	4·74	4·64	4·54	4·45	4·35	4·25	4·15	4·05	3·95
3	3·948	3·85	3·75	3·65	3·56	3·46	3·36	3·27	3·18	3·09	3·00
4	2·996	2·91	2·82	2·74	2·65	2·57	2·50	2·42	2·34	2·27	2·20
5	2·197	2·13	2·06	1·99	1·93	1·87	1·81	1·75	1·69	1·63	1·58
6	1·582	1·53	1·48	1·43	1·39	1·34	1·30	1·26	1·21	1·18	1·14
7	1·137	1·100	1·065	1·031	·998	·966	·935	·906	·878	·850	·823
8	·823	·798	·774	·750	·727	·704	·683	·662	·642	·623	·604
9	·604	·588	·570	·552	·537	·521	·507	·492	·478	·465	·452
10	·452	·439	·427	·415	·404	·394	·383	·373	·363	·353	·345
11	·345	·335	·324	·319	·310	·302	·295	·287	·280	·273	·267
12	·267	·260	·254	·248	·242	·237	·231	·226	·221	·216	·211
13	·211	·206	·202	·197	·193	·188	·184	·180	·176	·172	·169
14	·169	·165	·162	·159	·155	·152	·149	·146	·143	·140	·137
15	·137	·135	·132	·130	·127	·125	·122	·120	·118	·116	·113

$\frac{\Theta}{T}$	C_v	$\frac{\Theta}{T}$	C_v	$\frac{\Theta}{T}$	C_v
16	0·113	21	0·0502	26	0·0264
17	0·0945	22	0·0436	27	0·0236
18	0·0796	23	0·0382	28	0·0212
19	0·0677	24	0·0336	29	0·0190
20	0·0581	25	0·0298	30	0·0172

NOTE 13

Combination with Repetition

In Chapter XVII we have stated that the number of ways in which N_s particles can be distributed in A_s cells is equal to

$$\frac{(A_s+N_s-1)\,!}{(A_s-1)\,!\,N_s\,!}.$$

This can be derived as follows:

Let the cells be designated as $x_1, x_2, \dots, x_{A_s}$. A particular distribution can be represented by

$$x_1^{\alpha}\, x_2^{\beta} \dots\dots x_{A_s}^{\nu}, \qquad \dots \qquad (1)$$

where $\alpha, \beta, \dots, \nu$ are the number of particles in the cells $x_1, x_2, \dots x_{A_s}$ respectively and

$$\alpha+\beta+\dots+\nu = N_s \qquad \dots \qquad (2)$$

Now consider the product

$$(x_1^0+x_1^1+x_1^2+x_1^3+\dots+x_1^r+\dots)(x_2^0+x_2^1+x_2^2+\dots+x_2^r)\dots$$
$$(x^0_{A_s}+x^1_{A_s}+x^2_{A_s}+\dots+x^r_{A_s}+\dots),$$

where each factor consists of an infinite number of terms. In this product we have all possible combinations of the powers of $x_1, x_2, \dots, x_{A_s}$. Hence the number of ways of distributing N_s particles in the A_s cells is equal to the number of those terms of type (1) for which the condition (2) is satisfied. Now let $x_1 = x_2 = \dots\dots = x_{A_s} = x$. Then the number of combinations is equal to the coefficient of x^{N_s} in the expression

$$(x^0+x^1+x^2+\dots\dots+x^r+\dots\dots)^{A_s}$$

$$=\left(\frac{1}{1-x}\right)^{A_s} = (1-x)^{-A_s},$$

$$= 1 + A_s x + \frac{A_s(A_s+1)}{2\,!}x^2 + \dots\dots$$

$$+ \frac{A_s(A_s+1)(A_s+2)\dots(A_s+r-1)}{r\,!}x^r + \dots$$

Hence the required number is

$$\frac{A_s(A_s+1)(A_s+2)\dots\dots(A_s+N_s-1)}{N_s\,!} = \frac{(A_s+N_s-1)\,!}{(A_s-1)\,!\,N_s\,!}$$

A very simple proof of the relation is as follows:—
Consider the array

$$x_1\, a_2\, a_3\, x_4\, a_1\, x_2\, a_4\, a_6\, x_3\, a_5\, a_{N_s}\, x_5\, x_6 \cdots\cdots x_{A_s}$$

where x_1 denotes cell number 1 and a_2, a_3 denote particles 2 and 3 etc. The array symbolically means that particles 2, 3 are contained in cell 1, particle 1 in cell 4, particles 4 and 6 in cell 2 and so on; *i.e.* the particles contained in a cell are conventionally written on the right of the cell. In the array there are A_s+N_s terms. Keeping x_1 fixed in its place let us permute the remaining A_s+N_s-1 terms among themselves. This can be done in $(A_s+N_s-1)!$ ways. Out of these we reject those which consist merely in a permutation of the cells among themselves viz. $(A_s-1)!$ or a permutation of the particles among themselves viz. $N_s!$ because it is immaterial which particles are contained in which cells. Hence the total number of new arrangements is given by

$$\frac{(A_s+N_s-1)\,!}{(A_s-1)\,!\; N_s!}$$

NOTE 14

Integrals used in B. E.-and F. D.-Statistics.

The integrals used in §17·6 are of the form

$$I_n = \frac{1}{\Gamma(n+1)} \int\limits_0^\infty \frac{u^n\, du}{e^u - \gamma/f} \;.$$

When $f \gg 1$, this can be expanded as

$$I_n = \frac{1}{\Gamma(n+1)} \int\limits_0^\infty \sum_{r=0}^{\infty} \left(\frac{\gamma}{f}\right)^r e^{-(r+1)u}\, u^n\, du.$$

Since $$\int_0^\infty u^n\, e^{-(r+1)u}\, du = \frac{\Gamma(n+1)}{(r+1)^{n+1}},$$

we have $$I_n = \sum_{r=0}^{\infty} (\gamma/f)^r/(r+1)^{n+1},$$

or writing in full

$$I_n = 1 + \frac{\gamma}{2^{n+1}f} + \frac{\gamma^2}{3^{n+1}f^2} + \cdots \frac{\gamma^r}{(r+1)^{n+1}f^r} + \cdots$$

$$= 1 \pm \frac{1}{2^{n+1}f} + \frac{1}{3^{n+1}f^2} \pm \frac{1}{4^{n+1}f^3} + \cdots$$

the upper sign referring to B.E.-, the lower to F.D.-statistics.

When $f \simeq 1$.

It has been pointed out in the text, that for BE-statistics, the minimum value of $f=1$. We have then

$$I_{\frac{3}{2}}(1) = 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \dots = 2{\cdot}612,$$

which was utilised in §17·10.

For $f \ll 1$, we have only to consider Fermi-statistics, and find out the value of

$$I_n = \frac{1}{\Gamma(n+1)}\int_0^\infty \frac{u^n.\,du}{e^u+1/f},$$

for now $\gamma = -1$.

Let us take the function

$$V = \int_0^\infty \frac{du}{e^u+1/f}\ \phi'(u),$$

where $\phi(u)$ is a regular function of u, and vanishes for $u = 0$. Let us put $\log f = -\xi$. Since $f \ll 1$, $\xi > 0$. We can now write V as

$$V = \int_0^\xi \frac{du}{e^u+1/f}\,\phi'(u) + \int_\xi^\infty \frac{du}{e^u+1/f}\,\phi'(u)$$

$$= V_1 + V_2.$$

Writing $$\frac{1}{e^u+1/f} = f\left(1 - \frac{1}{1+f^{-1}e^{-u}}\right),$$

we have $$V_1 = f\int_0^\xi \phi'(u)\,du - f\int_0^\xi \frac{\phi'(u)}{1+f^{-1}e^{-u}}\,du$$

$$= f\,\phi(\xi) + V_3, \text{ where } V_3 = -f\int_0^\xi \frac{\phi'(u)}{1+f^{-1}e^{-u}}\,du.$$

Now for evaluating V_3, we put $u = \xi(1-t)$. Then we see that

$$V_3 = -\,\xi f\int_0^1 \frac{dt}{1+e^{\xi t}}\ \phi'(\xi-\xi t).$$

We may now change the upper limit to ∞. The error involved is of the order of $e^{-\xi} = f$ and is small, so that

$$V_3 = -\xi f\int_0^\infty \frac{dt}{1+e^{\xi t}}\ \phi'(\xi-\xi t).$$

For calculating V_2, we put $u = \xi(1+t)$. We have then

$$V_2 = \int_\xi^\infty \frac{du}{e^u+1/f}\,\phi'(u) = \xi f\int_0^\infty \frac{dt}{1+e^{\xi t}}\ \phi'(\xi+\xi t).$$

We have therefore

$$V_2+V_3=\xi f\int_0^\infty \frac{dt}{1+e^{\xi t}}\,\{\phi'(\xi+\xi t)-\phi'(\xi-\xi t)\}$$

$$=2f\sum\nolimits_{\nu=2,4,6..}\frac{\xi^{\nu}\phi^{\nu}(\xi)}{(\nu-1)!}\int_0^\infty\frac{t^{\nu-1}dt}{1+e^{\xi t}}$$

by Taylor's expansion, where $\phi^{\nu}(\xi)$ denotes νth differential of $\phi(\xi)$.

Now $$\int_0^\infty\frac{t^{\nu-1}dt}{1+e^{\xi t}}=\int_0^\infty t^{\nu-1}\left(e^{-\xi t}+e^{-2\xi t}+e^{-3\xi t}\ .\ .\ \right)dt$$

$$=\frac{(\nu-1)!}{\xi^{\nu}}\left(1-\frac{1}{2^{\nu}}+\frac{1}{3^{\nu}}-\frac{1}{4^{\nu}}+\ .\ .\ .\right)$$

$$=\frac{(\nu-1)!}{\xi^{\nu}}\,C_{\nu}$$

We know that $C_2=\frac{\pi^2}{12}$, $C_4=\frac{7}{8}\times\frac{\pi^4}{90}$, etc. We have therefore

$$V/f=\phi(\xi)+2\,\{C_2\phi^2(\xi)+C_4\phi^4(\xi)+\ .\ .\ .\}$$

For calculating I_n we have to put

$$\phi'(u)=\frac{u^n}{\Gamma(n+1)}\,,\ \text{hence}\ \phi(u)=\frac{u^{n+1}}{\Gamma(n+2)}$$

Hence

$$I_n/f=\frac{\xi^{n+1}}{\Gamma(n+2)}\left[1+2\left\{\frac{C_2n(n+1)}{\xi^2}+\frac{C_4(n+1)n(n-1)(n-2)}{\xi^4}+\ .\ .\ .\right\}\right]$$

Putting $n=\frac{1}{2}$ and $n=\frac{3}{2}$ respectively,

$$I_{\frac{1}{2}}/f=\frac{4}{3\sqrt{\pi}}\,\xi^{3/2}\left\{1+\frac{\pi^2}{8\xi^2}+\ .\ .\ .\right\}$$

$$I_{\frac{3}{2}}/f=\frac{8}{15\sqrt{\pi}}\,\xi^{5/2}\left\{1+\frac{5\pi^2}{8\xi^2}+\ .\ .\ .\right\}$$

NOTE 15

Wave-Mechanics and New Statistics

Before giving an account of the quantum mechanical treatment of statistics of an assembly of particles we shall give a brief sketch of the basic principles of wave-mechanics. This is necessary for a clearer understanding of what is to follow.

Since the time of Newton, we have been accustomed to the particle concept. In fact, Newton assumed that both matter as well as radiation consisted of particles. But about the year 1800, Young and Fresnel proved from study of diffraction and interference phenomena that light was a kind of wave motion. This theory held right upto 1900, when Planck showed, as explained in §15·32 that for explaining the laws of black-body radiation we have to suppose that light of frequency ν, consists of quanta of energy content $h\nu$. Thus an embarrassing position was created, viz., for explaining the phenomena of interference and diffraction we have to regard light as waves, while for explaining photo-electric phenomena, the laws of black-body radiation and the atomic spectra we have to regard light as consisting of atoms of energy. This dual concept of radiation is the great puzzle of modern physics.

In 1923, L. de Broglie showed that the dual concept of light may be extended to particles of matter as well. He was led to this conception from Einstein's idea that matter and energy are identical, in fact a particle of mass m may be supposed to possess the energy mc^2. From this, he concluded that since both matter-particles and photons are simply different forms of energy and are mutually convertible, their physical nature ought to be identical, and whatever properties may be deduced for one type, should *ipso facto* hold for the other type. Thus the dual conception of waves and particles may be extended to particles of matter as well. In fact, de Broglie succeeded in showing that a particle of mass m moving with the velocity v may be described as a wave of length $\lambda = h/mv$, a discovery which was soon found to explain successfully the experiments on electron reflection by Davisson and Germer, or the more direct experiments on electron diffraction by G. P. Thomson and others, which were inspired by de Broglie's discovery. Schrödinger showed that wherever the wavelength of particles is comparable with the dimensions of the space in which the particle moves as in the case of electron motion in the H-atom the wave-conception of matter has to be used in place of the particle-conception.

If the particles of classical dynamics are to be replaced by waves, we have naturally to find out corresponding substitutes for the dynamical concepts as well as for dynamical equations. It has been shown[1] that for the non-relativistic case, this is accomplished if we represent a free particle moving uniformly by a function ψ or its conjugate imaginary ψ^* such that

$$\psi = A\, e^{-2\pi i(\nu t - k_x x - k_y y - k_z z)} \quad . \quad . \quad . \quad . \quad (1)$$

---

[1] For proof see p. 882.

where
$$\left.\begin{aligned} h\nu &= mc^2 = \text{energy of the system} \\ hk &= mc = \text{momentum of the system;} \end{aligned}\right\} \quad . \quad . \quad (2)$$

A is the amplitude which may be a function of x, y, z.

The question now arises: how are we to find the ψ function in general when the particle is moving in any field of force? The answer to this important question was given by Schrödinger. We know that in classical mechanics the motion of any system is completely defined if the Hamiltonian H of the system is known. The motion can then be determined by solving the system of differential equations

$$\frac{\partial q_r}{\partial t} = \frac{\partial H}{\partial p_r}, \quad \frac{\partial p_r}{\partial t} = -\frac{\partial H}{\partial q_r}, \quad . \quad . \quad . \quad . \quad (3)$$

(called Hamiltonian equations) subject to the given initial conditions. The Hamiltonian H is a function of the p's and q's, the generalised momentum and position coordinates. Schrödinger showed that the wave function ψ for the system is obtained as the solution of the differential equation (Schrödinger's equation)

$$\frac{ih}{2\pi}\frac{\partial\psi}{\partial t} = H\left(q_r, -\frac{ih}{2\pi}\frac{\partial}{\partial q_r}\right)\psi, \quad . \quad . \quad . \quad (4)$$

where h is the Planck constant, and the conjugate equation

$$-\frac{ih}{2\pi}\frac{\partial\psi^*}{\partial t} = H\left(q_r, \frac{ih}{2\pi}\frac{\partial}{\partial q_r}\right)\psi^* \quad . \quad . \quad . \quad (5)$$

where every p_r occurring in H has been replaced by the operator $-\frac{ih}{2\pi}\frac{\partial}{\partial q_r}$ in the equation for ψ and by $\frac{ih}{2\pi}.\frac{\partial}{\partial q_r}$ in the equation for ψ^*. If H does not contain the time explicitly, the above equation may be immediately integrated. We have

$$\psi = \psi(q_r).\, e^{-2\pi iEt/h} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $\psi(q_r)$ satisfies the equation

$$H\left(q_r, -\frac{ih}{2\pi}\frac{\partial}{\partial q_r}\right)\psi(q_r) = E\,\psi(q_r). \quad . \quad . \quad . \quad (7)$$

We are to seek only those solutions of Schrödinger's equation which satisfy certain conditions, i. e., $\psi \to 0$ at infinity, and $\int\psi\psi^* dv$ integrated over all space is finite, but we need not enter here into these details. In general we shall obtain a number of independent solutions ψ_1, ψ_2, etc., each corresponding to a definite value of the energy parameter E. We shall speak of each ψ_n as an eigen-function ψ_n of the corresponding eigen-value of the energy E_n. As a simple illustration of the solution of Schrödinger's equation, we shall deduce the result given above for a free particle. In this case

$$H = \frac{1}{2m}\left(p_x^2+p_y^2+p_z^2\right), \quad . \quad . \quad . \quad . \quad (8)$$

and Schrödinger's equation becomes

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x, y, z) = E\,\psi(x, y, z). \quad . \quad (9)$$

We first investigate the possibility of writing the solution in the form

$$\psi(x, y, z) = X(x)\,Y(y)\,Z(z), \quad . \quad . \quad . \quad (10)$$

where $X(x)$ is a function of x alone, $Y(y)$ of y alone, and $Z(z)$ of z alone. Equation (9) can now be written as

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} = -\frac{8\pi^2 m}{h^2}E \quad . \quad . \quad (11)$$

A simple argument now shows that equation (11) can be broken up into the three equations

$$\left.\begin{aligned} \frac{1}{X}\frac{\partial^2 X}{\partial x^2} = -\frac{8\pi^2 m}{h^2}E_x, \quad \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} = -\frac{8\pi^2 m}{h^2}E_y,\\ \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} = -\frac{8\pi^2 m}{h^2}E_z \quad . \end{aligned}\right\} \quad . \quad (12)$$

where E_x, E_y, E_z are three constants satisfying the condition

$$E_x + E_y + E_z = E. \quad . \quad . \quad . \quad . \quad (13)$$

The solutions of the three equations in (12) are

$$\left.\begin{aligned} X &= A_1 e^{2\pi i k_x x} + B_1 e^{-2\pi i k_x x}\\ Y &= A_2 e^{2\pi i k_y y} + B_2 e^{-2\pi i k_y y}\\ Z &= A_3 e^{2\pi i k_z z} + B_3 e^{-2\pi i k_z z} \end{aligned}\right\} \quad . \quad . \quad . \quad (14)$$

where $$4\pi^2(k_x^2+k_y^2+k_z^2) = 4\pi^2 k^2 = \frac{8\pi^2 m}{h^2}(E_x+E_y+E_z).$$

Or $$4\pi^2 k^2 = \frac{8\pi^2 m}{h^2}E = 4\pi^2 m^2 v^2/h^2$$

or $$k = mv/h, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

which is the same as the second equation (2). The first terms in equation (14) represent a wave moving in the positive direction. Taking these terms only and adding the time factor we get equation (1). Since there is no restriction to the values which k_x, k_y, k_z can assume, the energy has a continuous range of values.

The physical significance of regarding p as an operator in quantum mechanics was brought out by Heisenberg and Bohr. The former, starting from a point of view different from that of Schrödinger, showed that the basis of quantum mechanics lay in the operational equation

$$q_r p_s - p_s q_r = \frac{ih}{2\pi}\,\delta_{rs}\,. \quad . \quad . \quad . \quad (16)$$

where

$$\delta_{rs} = 1 \text{ for } r = s,$$
$$\delta_{rs} = 0 \qquad r \neq s.$$

Therefore q_r and p_r no longer commute $(q_r p_r \neq p_r q_r)$ contrary to what we get in the classical theory. We immediately verify that (16) is the same as Schrödinger condition

$$p_r = -\frac{ih}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

as follows. For any ψ

$$(q_r p_r - p_r q_r)\psi = -\frac{ih}{2\pi}\left(q_r \frac{\partial}{\partial q_r} - \frac{\partial}{\partial q_r}\cdot q_r\right)\psi = \frac{ih}{2\pi}\,\psi$$

from which (16) follows immediately.

Bohr was the first to clearly realise the physical basis of (16). He showed that the non-commutability relation is a consequence of the fact that even in principle it is inherently impossible to devise an experiment for the exact simultaneous measurement of both q_r and p_r. In fact the uncertainties $\triangle q_r$ in the measurement of q_r and $\triangle p_r$ in the simultaneous measurement of p_r are shown from (16) to be connected by the relation

$$\triangle q_r \cdot \triangle p_r \geqq h/2\pi. \quad . \quad . \quad . \quad . \quad . \quad (18)$$

By considering several ideal experiments Bohr, and following him others, have been able to verify (18) from elementary physical principles. As the classical theory is the limiting case of $h \to 0$, so $\triangle q_r \, \triangle p_r \simeq 0$ and therefore the errors in the simultaneous measurement of q_r and p_r vanish.

The particle in a box—Let us now study the case of a particle constrained to move inside a rectangular box of edges a, b and c. We can visualise that the particle moves in a potential field which is zero inside and infinite outside the box. Taking the origin in one corner of the box, the Hamiltonian of the particle can be written as

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V(x, y, z), \quad . \quad . \quad . \quad (19)$$

where $V(x, y, z) = 0$ for $0 < x < a$, $0 < y < b$, $0 < z < c$ and infinite outside these limits. Let us represent the potential function as

$$V(x, y; z) = V_x(x) + V_y(y) + V_z(z).$$

where $V_x(x) = 0$ for $0<x<a$ and equal to infinity outside this range and the functions $V_y(y)$ and $V_z(z)$ show a similar behaviour for the specified ranges of y and z respectively. The wave equation is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}\{E - V_x(x) - V_y(y) - V_z(z)\}\psi = 0. \quad (20)$$

As in the case of the free particle we can solve this equation by the same substitution (10), the differential equation for $X(x)$ being

$$\frac{\partial^2 X(x)}{\partial x^2} + \frac{8\pi^2 m}{h^2}\left(E_x - V(x)\right)X = 0 \; . \; . \; . \; . \quad (21)$$

We have two similar equations for $Y(y)$ and $Z(z)$ with the condition that

$$E_x + E_y + E_z = E. \; . \; . \; . \; . \quad (22)$$

The general solution of (21) is

$$X = A \sin\,(k_x x + a),$$

where A, k_x and a are constants, k_x being related to E_x by the equation

$$k_x{}^2 = \frac{8\pi^2 m}{h^2} E_x.$$

Similarly for Y and Z. The complete solution is given by

$$\psi = A \sin\,(k_x x + a) \sin\,(k_y y + \beta) \sin\,(k_z z + \gamma) \; . \; . \quad (23)$$

where A, k_x, k_y, k_z, a, β, γ are constants, being connected by the equation

$$k_x{}^2 + k_y{}^2 + k_z{}^2 = \frac{8\pi^2 m}{h^2}(E_x + E_y + E_z) = \frac{8\pi^2 m}{h^2} E. \quad (24)$$

We must now consider the boundary conditions which will be imposed by the presence of the walls of the box which have been represented in the problem by the existence of a potential at the walls. In the region $x<0$ or $x>a$, equation (21) becomes

$$\frac{\partial^2 X}{\partial x^2} = \beta^2 X, \; . \; . \; . \; . \; . \; . \quad (21')$$

where $$\beta^2 = \frac{8\pi^2 m}{h^2}\left\{ V(x) - E \right\} = \text{infinity}.$$

The solution of (21′) which vanishes at $x = \infty$ is $X = Be^{-\beta x}$ and since $\beta = \infty$, this vanishes for all values of $x>a$. Similarly the solution must vanish for all negative values of x. Hence the boundary conditions to be satisfied by the solution (23) are that it must vanish at $x = 0$, $y = 0$ and $z = 0$. This makes $a = \beta = \gamma = 0$. Also it must vanish at $x = a$, $y = b$, $z = c$. Hence we must have

$$k_x = \pi n_x/a, \quad k_y = \pi n_y/b, \quad k_z = \pi n_z/c,$$

where n_x, n_y and n_z are integers. Hence

$$E = \frac{h^2}{8m}\left[\left(\frac{n_x}{a}\right)^2 + \left(\frac{n_y}{b}\right)^2 + \left(\frac{n_z}{c}\right)^2\right]. \quad . \quad . \quad (24')$$

n_x, n_y and n_z can assume all integral values which satisfy equation (24′). Corresponding to each set of values of n_x, n_y and n_z there will be one independent wave-function. If there is more than one set of values of n_x, n_y, n_z satisfying (24′) there will be more than one eigen-function corresponding to the same eigen-value E. The state is then said to be degenerate, the degree of degeneracy being measured by the number of eigen-functions belonging to the same eigen-value. In the present case if no two edges of the box a, b and c are in the ratio of integers, the energy levels corresponding to various sets of values of the three quantum numbers are all different, with one and only one independent eigen-function associated with each. If, however, there exists an integral relation among a, b and c, there will occur certain values of the energy corresponding to two or more distinct sets of values of the three quantum numbers n_x, n_y, and n_z and to two or more independent eigen-functions.

We will now calculate the number of different eigen-functions or steady quantum states having eigen-values of the energy lying within a given range, say ϵ_s to $\epsilon_s + d\epsilon_s$. Since each integral combination of n_x, n_y, n_z satisfying (24) gives rise to an independent eigen-function, the required number, using arguments similar to those of (§17·2), is

$$G_s = \frac{2\pi V(2m)^{3/2}\,\epsilon_s^{1/2}\,d\epsilon_s}{h^3} \quad . \quad . \quad . \quad . \quad (25)$$

In case the particle has a spin, the above expression is to be multiplied by $g=2j+1$, where j is the spin moment of the particle in units of $h/2\pi$. It may be recalled that equation (25) is the same expression which we have used for the number of phase-cells in the energy range lying between ϵ_s and $\epsilon_s+d\epsilon_s$.

Let us now go back to the Schrödinger equation and consider the case of two systems having negligible interaction. Let their Hamiltonians be H_1 and H_2 respectively. The Hamiltonian H of the combined system (or assembly) will be

$$H=H_1+H_2\,, \quad . \quad . \quad . \quad . \quad . \quad (26)$$

where the interaction term H_{12} has been assumed to be negligible. The Schrödinger equation of this assembly

$$H\psi = E\psi. \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

becomes

$$(H_1+H_2)\psi = (E_1+E_2)\psi,$$

or

$$(H_1-E_1)\psi+(H_2-E_2)\psi = 0, \quad . \quad . \quad . \quad . \quad (27')$$

and is thus separable into two parts, one for the first system and the other for the second. Therefore ψ will be of the product form $\psi(1|E_1)$. $\psi(2|E_2)$, where $\psi(1|E_1)$ denotes the wave-function of the first system in the energy state E_1 and $\psi(2|E_2)$ denotes the wave-function of the other for its energy value E_2. $\psi(1|E_1)$ is a solution of the equation $(H_1-E_1)\,\psi=0$ and $\psi(2|E_2)$ is the solution of $(H_2-E_2)\psi=0$. The product $\psi=\psi(1|E_1)\;\psi(2|E_2)$ satisfies equation (27) for

$$\begin{aligned}(H_1-E_1)\psi+(H_2-E_2)\psi &= (H_1-E_1)\;\psi(1|E_1)\;\psi(2|E_2)\\ &\quad+(H_2-E_2)\;\psi(1|E_1)\;\psi(2|E_2)=0.\end{aligned}$$

Let us now suppose that the two systems are similar, i.e., physically indistinguishable (say both are H atoms). For this case of similar systems, there emerges a new and interesting point which will lead to far reaching consequences. The energy state E_1+E_2 of the combined system is realisable in two ways :

(*a*) First system in the energy state E_1 and the wave-function $\psi(1|E_1)$	Second system in the energy state E_2 and the wave-function $\psi(2|E_2)$

and thus $\psi_a=\psi(1|E_1)\;\psi(2|E_2)$.

(*b*) First system in the energy state E_2 and the wave-function $\psi(1|E_2)$	Second system in the energy state E_1 and the wave-function $\psi(2|E_1)$

and thus $\psi_b=\psi\,(1|E_2).\;\psi\,(2|E_1)$.

These two ways are physically indistinguishable. Thus the energy state E_1+E_2 of the combined system is degenerate for we have two independent wave-functions ψ_a and ψ_b representing it. This type of degeneracy is called *exchange degeneracy* and it is principally due to Heisenberg that we owe the full realisation of its significance. As the Schrödinger equation is linear in ψ, it follows that any linear combination of ψ_a and ψ_b will also satisfy the differential equation and represent the same energy state E_1+E_2. Consider for example the combinations

$$\begin{aligned}\psi(S)&=\psi(a)+\psi\,(b)=\psi(1|E_1)\;\psi(2|E_2)+\psi\,(1|E_2)\;\psi(2|E_1)\\ \psi(A)&=\psi(a)-\psi(b)=\psi(1|E_1)\;\psi(2|E_2)-\psi(1|E_2)\;\psi(2|E_1).\end{aligned}\tag{28}$$

$\psi(A)$ may be written in the determinant form

$$\psi(A)=\begin{vmatrix}\psi\,(1|E_1) & \psi\,(2|E_1)\\ \psi\,(1|E_2) & \psi\,(2|E_2)\end{vmatrix}\quad .\quad .\quad .\quad .\tag{28'}$$

and $\psi(S)$ is the same determinant in which all the terms are taken with the positive sign, i.e., a permanent. $\psi(S)$ is symmetrical in the two systems, i.e., an interchange of the two systems (putting 1 in place of 2 and 2 in place of 1) leaves it unchanged. On the other hand an interchange of the two systems changes the sign of $\psi(A)$, i.e., if in the expression for $\psi(A)$, we put 1 in place of 2 and 2 in place of 1, we obtain $-\psi(A)$. Because of this property $\psi(A)$ is called antisymmetrical in the two systems.

From what has been said so far it would seem that both wave-functions $\psi(A)$ and $\psi(S)$ or any linear combination of them will represent the system in the energy state E_1+E_2 and indeed it would be so were it not for a restriction of entirely non-classical nature imposed by the following fundamental principle of quantum mechanics. The principle states that *if any assembly composed of any number of similar systems, interacting mutually and also with its surroundings, is at some time to be represented by a wave function ψ_0 possessing certain symmetric properties with respect to the interchange of the undistinguishable systems constituting it, then wave-function representing it at any later time will also possess the same symmetric properties as ψ.*

The proof of this important theorem is as follows. The Hamiltonian H of the assembly will be of the form

$$H_x = \frac{1}{2m}\left\{ \Sigma p_{x_1}{}^2 + \Sigma p_{x_2}{}^2 + \cdots \right\} + V(x_1, y_1, z_1, x_2, y_2, z_2). \quad (29)$$

The potential energy term V must be symmetrical among the systems, i.e., V remains unchanged when say x_1, y_1, z_1 are interchanged with x_2, y_2, z_2 respectively. This simply expresses the fact that the systems are similar. Thus we see that H is symmetrical in the systems, for the part $\{\ \}$ is obviously symmetrical. Let ψ be a solution of the Schrödinger equation

$$-\frac{h}{2\pi i}\frac{\partial\psi}{\partial t} = H\psi. \quad . \quad . \quad . \quad . \quad (30)$$

Now ψ will be a function of the coordinates of all the systems, i.e.,

$$\psi \equiv \psi\,(x_1, y_1, z_1;\ x_2, y_2, z_2 \cdots\cdots).$$

Let $P\psi$ denote the ψ obtained by a certain definite permutation among the systems in ψ.

As H is symmetrical in the systems,

$$P\,H = H\,P,$$

and therefore we have multiplying (30) by P,

$$-\frac{h}{2\pi i}\frac{\partial}{\partial t}(P\psi) = P\,(H\,\psi) = H\,(P\,\psi), \quad . \quad (31)$$

i.e., $P\psi$ also satisfies the Schrödinger equation. Take the case that ψ is symmetrical at a particular instant say t_0. Then

$$P\,\psi = \psi, \qquad \text{or } (P\psi - \psi) = 0. \quad . \quad . \quad . \quad (32)$$

Now from (30) and (31) we have

$$\frac{\partial}{\partial t}(P\psi) = \frac{\partial\psi}{\partial t}, \quad \text{or } \frac{\partial}{\partial t}\{P(\psi) - \psi\} = 0. \quad . \quad . \quad . \quad (33)$$

Thus if (32) holds at one instant t_0, (33) tells us that it holds at a slightly later instant and thus by induction it holds at all times. Therefore if a wave function is initially symmetrical, it always remains symmetrical.

Similarly the theorem could be proved for the antisymmetrical case. We therefore see that the symmetry property of the wave-functions is fixed once for all and is the property only of the systems constituting the assembly.

If there be an assembly consisting of similar systems, then the wave-function representing any state of the assembly will either be symmetrical or antisymmetrical in every pair of particles. It will be seen later that the symmetrical case corresponds to Bose-Einstein statistics, and the antisymmetrical to Fermi-Dirac statistics. Now it has been shown by Pauli[1] that it is a consequence of the general features of the quantum theory that elementary particles with half-integral spins (in units of $h/2\pi$) are governed by the Fermi-Dirac statistics and particles with integral spins must obey the Bose-Einstein statistics. This is also supported by experimental evidence. The symmetry property of a complex particle can be derived in terms of the particles of which it is composed. The wave-functions must be symmetrical in a particle which is composed of elementary particles of integral spins only or if the number of elementary particles of half-integral spin is even. However, if the complex nucleus contains an odd number of elementary particles of half-integral spins, the assembly will have antisymmetrical wave-function. Protons, neutrons and electrons possess a spin moment equal to $\frac{1}{2}h/2\pi$ and wave functions are anti-symmetrical in them and they obey the Fermi-Dirac statistics while photons which have zero spin obey the Bose-Einstein statistics. The helium nucleus of mass 4 contains two protons and two neutrons. The wave function changes sign if one proton is interchanged with another proton. Hence the sign must remain the same if a pair of protons or a proton and a neutron is interchanged with a pair of protons or a proton and a neutron. It is obvious, therefore, that the wave-functions must be symmetrical in the helium nucleus of mass 4. On the other hand the helium nucleus of mass 3 contains two protons and one neutron. Hence the wave-function must be antisymmetrical in the helium nucleus of mass 3. Similarly, it must be antisymmetric in the helium atom of atomic weight 3, as it contains five elementary particles of half-integral spins, but symmetric in the hydrogen atom of atomic weight 1, as the latter contains two particles of half-integral spins. The symmetry property of more complex particles can be derived from similar considerations. It must be emphasised that while considering the symmetry properties, account must also be taken of the spin coordinates.

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[1] W. Pauli, *Phys. Rev.*, **58**, 716, 1940.

Let us now consider equation (28). $\psi(A)$ vanishes if $E_1=E_2$. Hence if there is only one wave function corresponding to each value of the energy two (or more) similar particles with half-integral spins cannot be in the same energy state. This is known as Pauli's exclusion principle. $\psi(S)$, however, has still a value, viz.,

$$\psi(S) = \psi(1|E_1)\,.\,\psi(2|E_2).$$

This means that particles with integral spins do not obey Pauli's exclusion principle and there can be two (or more) particles occupying the same energy state even in the non-degenerate case.

We shall now consider the degenerate case. For simplicity we shall first assume that there are only three distinct wave functions corresponding to the energy value E_1. The wave-functions corresponding to the first particle are $\psi^{(1)}(1|E_1), \psi^{(2)}(1|E_1)$ and $\psi^{(3)}(1|E_1)$ and corresponding to the second particle they are $\psi^{(1)}(2|E_1)$, $\psi^{(2)}(2|E_1)$ and $\psi^{(3)}(2|E_1)$. From these we can build three independent antisymmetrical wave-functions for the assembly of two particles. They are

$$\psi_1(A) = \begin{vmatrix} \psi^{(1)}(1|E_1) & \psi^{(1)}(2|E_1) \\ \psi^{(2)}(1|E_1) & \psi^{(2)}(2|E_1) \end{vmatrix}; \quad \psi_2(A) = \begin{vmatrix} \psi^{(2)}(1|E_1) & \psi^{(2)}(2|E_1) \\ \psi^{(3)}(1|E_1) & \psi^{(3)}(2|E_1) \end{vmatrix}$$

$$\psi_3(A) = \begin{vmatrix} \psi^{(3)}(1|E_1) & \psi^{(3)}(2|E_1) \\ \psi^{(1)}(1|E_1) & \psi^{(1)}(2|E_1) \end{vmatrix} \quad . \quad . \quad . \quad (34)$$

It will be observed that in (34) elements in each column of the determinant are made up of the different ψ-functions of one of the particles. Each row is characterised by a different upper suffix of the ψ-function. Hence the total number of independent wave-functions for the assembly is the number of combinations of two upper suffixes out of a total of three upper suffixes.

Let us now consider the more general case. We shall assume that the number of independent wave-functions corresponding to the energy state ϵ_s is A_s and that there are N_s similar particles occupying the energy state ϵ_s. We shall calculate the total number of wave-functions corresponding to this assembly. A typical wave-function for the assembly is represented by the following determinant of order N_s:

$$\begin{vmatrix} \psi^{(a)}(1|\epsilon_s) & \psi^{(a)}(2|\epsilon_s)\ldots\ldots\psi^{(a)}(N_1|\epsilon_s) \\ \psi^{(b)}(1|\epsilon_s) & \psi^{(b)}(2|\epsilon_s)\ldots\ldots\psi^{(b)}(N_1|\epsilon_s) \\ \psi^{(c)}((1|\epsilon_s) & \psi^{(c)}(2|\epsilon_s)\ldots\ldots\psi^{(c)}(N_1|\epsilon_s) \\ \vdots & \vdots \qquad\qquad\qquad \vdots \\ \psi^{(d)}(1|\epsilon_s) & \psi^{(d)}(2|\epsilon_s)\ldots\ldots\psi^{(d)}(N_1|\epsilon_s) \end{vmatrix} \ldots \quad (34')$$

The number of upper suffixes (*a*), (*b*) ..... is A_s and as before each column consists of wave-functions corresponding to one of the N_s particles and each row is characterised by a different upper suffix. The wave-function vanishes identically if two rows have the same upper suffixes. Hence the number of different independent wave-functions of the assembly will be equal to the number of ways of choosing N_s different upper suffixes out of a total A_s upper suffixes. This number is clearly

$$ {}^{A_s}C_{N_s} = \frac{A_s!}{N_s!\,(A_s-N_s)!} \quad . \quad . \quad . \quad . \qquad (35)$$

Let us now determine the number of different independent wave-functions for the assembly when the particles composing the assembly have integral spins. The wave-function describing the state of the assembly has now to be symmetrical in the systems. A typical wave-function is of the form (34′) with the sign of each term taken positive. Due to this the wave-function does not vanish even when two or more upper suffixes have the same value. Hence the number of different independent wave-functions of the assembly will be equal to the number of ways of choosing N_s upper suffixes out of a total of A_s upper suffixes when two or more upper suffixes in any combination can have the same value. This process is known in algebra as combination with repetition, and it can be proved[1] that the total number of combinations is given by

$$\frac{(A_s+N_s-1)!}{N_s!\,(A_s-1)!} \sim \frac{(A_s+N_s)}{N_s!\,A_s!} \quad . \quad . \quad . \qquad (36)$$

This number is much larger than the number according to (35), but is much smaller (as we shall see presently) than the number allowed according to the classical statistics.

Consider now an assembly consisting of a very large number of N similar systems. Let the energy levels of the systems be denoted by

$$\epsilon_0,\ \epsilon_1,\ \epsilon_2, \ldots\ldots, \epsilon_s, \ldots\ldots$$

Any statistical state of the assembly can be specified by a set of positive integers (including zero) N_0, N_1, ..., N_s,.., where N_s denotes the number of systems in their ϵ_s energy level. We shall always have

$$N = \Sigma_s N_s, \quad U = \Sigma_s N_s\,\epsilon_s \quad . \quad . \quad . \quad . \qquad (37)$$

where U is the total energy of the assembly.

The specification of the energy of the assembly by (37) and in fact the assigning of individual stationary states and energies to the systems separately assumes that they are ***practically independent*** systems, i.e., their mutual interaction is very weak, each system pursuing its own motion undisturbed for the greater part of the time.[1] Therefore, the Hamiltonian of the assembly will be (to a first approximation) a sum of the separate Hamiltonians of the systems and hence Schrödinger's equation for the assembly will be separable corresponding to each separate Hamiltonian.

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[1] See Note 13.

Any wave function of the assembly which is anti-symmetrical in all the systems would take the form of a determinant—a typical example being

$$\begin{vmatrix} \psi^{(1)}(1|\epsilon_0) & \psi^{(1)}(2|\epsilon_0)\ldots\ldots & \psi^{(1)}(N|\epsilon_0). \\ \psi^{(2)}(1|\epsilon_0) & \psi^{(2)}(2|\epsilon_0)\ldots\ldots & \psi^{(2)}(N|\epsilon_0) \\ \psi^{(1)}(1|\epsilon_1) & \psi^{(1)}(2|\epsilon_1)\ldots\ldots & \psi^{(1)}(N|\epsilon_1) \\ \psi^{(1)}(1|\epsilon_3) & \psi^{(1)}(2|\epsilon_3)\ldots\ldots & \psi^{(1)}(N|\epsilon_3) \\ & & \\ \psi^{(1)}(1|\epsilon_u) & \psi^{(1)}(2|\epsilon_u)\ldots\ldots & \psi^{(1)}(N|\epsilon_u) \end{vmatrix} \qquad (38)$$

This corresponds to the characteristic

$N_0 = 2, N_1 = 1, N_2 = 0, \ldots\ldots N_u = 1$ and $U = 2\epsilon_0 + \epsilon_1 + \epsilon_3 + \ldots + \epsilon_u$.

The anti-symmetrical wave function vanishes identically if any two rows of the determinant be equal, i.e. if any two systems have the same wave functions (or states). Generalising equation (35) it follows that the number of anti-symmetrical wave functions corresponding to a specified statistical distribution is

$$P_F = \prod_s \frac{A_s\,!}{N_s\,!\,(A_s - N_s)\,!} \quad . \quad . \quad . \quad (39)$$

Similarly for the symmetrical case, the number of wave-functions of the assembly corresponding to a statistical distribution is

$$P_{B.E.} = \prod_s \frac{(A_s + N_s - 1)\,!}{(A_s - 1)\,!\,N_s\,!} \sim \prod_s \frac{(A_s + N_s)\,!}{A_s\,!\;N_s\,!} \quad . \quad . \quad . \quad (40)$$

The expression (39) was obtained by Fermi[2] in 1926. Almost simultaneously Dirac[3] obtained the same result from the symmetry considerations of the wave functions. The statistics embodied in (39) is called Fermi-Dirac or briely FD -statistics. Similarly the statistics embodied in (40) is called Bose[4]-Einstein[5] or BE-statistics.

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[1] If the interaction is altogether absent the systems will not form a connected assembly and obviously cannot possess definite equilibrium laws.

[2] Fermi, *Zeits., f. Physik*, **36**, 902, 1926.

[3] Dirac, *Proc. Roy. Soc.*, **112**, 661, 1926.

[4] Bose, *Zeits. f. Physik*, **26**, 178, 1924.

[5] Einstein, *Sitzungsber. Preuss. Akad.*, p. 261, 1924.

For the sake of comparison we shall evaluate also the value of P according to classical statistics. Here the particles are considered distinguishable and we do not have to apply any symmetry considerations to the wave functions of the assembly.

We have seen that if two systems 1 and 2 have the eigen-functions $\psi(1|E_1)$, $\psi(2|E_2)$ and the eigen-energies E_1, E_2, the eigen-function for the combined assembly is given by their product, viz.

$$\psi(1|E_1)\ .\ \psi(2|E_2).$$

We can generalise this theorem for the assembly specified by equation (37). The eigen-function would be

$$\begin{aligned}\psi = \psi\,(1|\epsilon_0)\,.\,\psi(2|\epsilon_0).\ .\ .\ .\ \ &\psi(N_0|\epsilon_0)\times\\ \psi(\overline{N_0+1}|\epsilon_1)\ .\ .\ .\ .\ \ &\psi(\overline{N_0+N_1}|\epsilon)\times\\ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ &.\ \ .\\ .\ \ .\ \ .\ \ &\psi(\overline{N_0+N_1+\ldots\ +N_s}|\epsilon_s)\ .\qquad .\quad .\quad (41)\end{aligned}$$

We have assumed above that there is only one eigen-function corresponding to each eigen-value. It can, however, be easily seen that this is not the only eigen-function for the state of the assembly specified by (37). For example, we can take any two particles from rows (1) and (2), e.g. we interchange the (N_0+1)th. particle with the second particle, i.e. $\psi(2|\epsilon_0)$ which is a function of $x_2, y_2, z_2, \epsilon_0$ is now replaced by $\psi(\overline{N_0+1}|\epsilon_0)$ which is the same function of x_{N_0+1} y_{N_0+1}, z_{N_0+1}, ϵ_0 and $\psi(\overline{N_0+1}|\epsilon_1)$ is now replaced by $\psi(2|\epsilon_1)$. The new ψ-function obtained in this way represents the assembly equally well. Let us now see how many distinct ψ-functions we can obtain in this way. It can easily be seen that the number is

$$P = \frac{N!}{N_0!\,N_1!\,N_2!\ldots N_s!}, \quad .\quad .\quad .\quad .\quad (42)$$

because if the systems had distinct eigen-energies, the number would be obtained by the permutation of the systems amongst themselves (N coordinate systems). But N_0 of them are in the same energy state ϵ_0. By permuting these N_0 amongst themselves, no new eigen-function arises. Hence the above number is to be divided by $N_0!$ and for a similar reason by $N_1!$, $N_2!$, etc.

Further, if the energy states themselves are degenerate, i.e. A_s distinct eigen-functions possess the same eigen-values ϵ_s (A_s is generally called the weight of the state ϵ_s), then clearly the number of distinct wave functions of the assembly for the given statistical distribution is

$$P = N!\prod \frac{A_s^{N_s}}{N_s!} \quad .\quad .\quad .\quad .\quad .\quad (43)$$

The factor $A_s^{N_s}$ arises in the following way: as there are A_s eigen functions for the eigen-energy ϵ_s, each system in ϵ_s-state can be represented by any one of the A_s eigen-functions, i.e., in A_s ways. Hence N_s systems can be represented in $A_s^{N_s}$ ways. P_c therefore is the total number of distinct wave-functions for the specified statistical distribution. By taking a numerical example it can now be verified that P_c is much greater than the value of P in the other two statistics. However, the number of wave functions representing the given state of the assembly will be actually much smaller than this, being either symmetrical or antisymmetrical as already discussed.

We now postulate that all states (or eigen-functions) realisable by an assembly have the same á priori probability. The assumption is capable of a formal justification as has been shown by Neumann[1] and also by Dirac.[2] Thus the number of ways (eigen-functions) of realising a specified statistical distribution of the assembly is

$$P_C = N! \prod_s \frac{(A_s)^{N_s}}{N_s!} \qquad \text{Classical}$$

$$P_F = \prod_s \frac{A_s!}{N_s!\,(A_s-N_s)!} \qquad \text{Fermi-Dirac}$$

$$P_B = \prod_s \frac{(A_s+N_s-1)!}{N_s!\,(A_s-1)!} \qquad \text{Bose-Einstein.}$$

NOTE 16

Method of Darwin and Fowler

Darwin and Fowler sought to avoid uncertainty in the statistical definition of entropy by calculating the average value of the partition-sums. We shall illustrate the method by taking the simple case of an assembly consisting of two sets of Planck oscillators A and B. Let the energy quanta of the two systems be ϵ and η respectively. Let us suppose that the total number of oscillators of the two types A and B are N_a and N_b respectively. We make the assumption that the oscillators in the two systems can have energies equal to any integral multiple of the quanta ϵ and η respectively. Let a_0, a_1, $a_2 \ldots \ldots a_r \ldots$ be the number of oscillators of the first type possessing the energies 0, ϵ, $2\epsilon, \ldots \ldots r\epsilon \ldots$ Similarly let b_0, $b_1 \ldots b_s$ denote the corresponding quantities for the second type of oscillators. Then we have the conditions

$$\Sigma_r a_r = N_a, \quad \Sigma_s b_s = N_b, \quad \Sigma_r r\, a_r\, \epsilon + \Sigma_s s b_s \eta = E. \qquad (1)$$

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[1] *Gött. Nach.*, p. 245, (1927).

[2] *Proc. Camb. Phil. Soc.*, 25, 62, 1928.

Let us now find out the number of ways in which this particular distribution can be obtained. It is equal to the number of permutations which are possible when out of N_a substances we have to choose the groups $a_0, a_1, \ldots \ldots a_r \ldots \ldots$ multiplied by the number of possible permutations in groups of $b_0, b_1 \ldots \ldots b_s$ in the second system of N_b substances. This number is equal to[1]

$$\frac{N_a!}{a_0!\, a_1! \ldots} \cdot \frac{N_b!}{b_0!\, b_1! \ldots}.$$

The total number of complexions with the energy E is given by the expression

$$C = \sum_{a,b} \frac{N_a!\; N_b!}{\prod a_r!\, \prod b_s!} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

summed up for all values of a_r and b_s subject to the conditions (1).

Let us introduce the quantities f_a, f_b and F, defined by the relations

$$\left.\begin{aligned} f_a &= 1+z^{\epsilon}+z^{2\epsilon}+\ldots\ldots+z^{r\epsilon}+\ldots\ldots = \frac{1}{1-z^{\epsilon}} \\ f_b &= 1+z^{\eta}+z^{2\eta}+\ldots\ldots+z^{r\eta}+\ldots\ldots = \frac{1}{1-z^{\eta}}. \end{aligned}\right\} \quad . \quad . \quad (3)$$

$$F = f_a^{N_a} \cdot f_b^{N_b} = (1+z^{\epsilon}+z^{2\epsilon}+\ldots)^{N_a} \cdot (1+z^{\eta}+z^{2\eta}+\ldots)^{N_b} \quad (4)$$

where z stands for the quantity $e^{-1/kT}$ as will be proved later.

By taking the help of the well-known polynomial theorem it will be seen that the term containing z^E in the infinite series (4) is given by

$$\sum_{a,b} \frac{N_a!\; N_b!}{\prod a_r!\, \prod b_s!}\, z^{\Sigma r a_r \epsilon + \Sigma s b_s \eta},$$

where the summation is taken for all values of a_r and b_s subject to the conditions (1). On comparing with (2) we see that the number of complexions C which we want to find out occurs as the coefficient of z^E in the expansion (4). We can evaluate C, by using Cauchy's theorem of residues in the theory of complex integration. In fact it can be shown that

$$C = \frac{1}{2\pi i} \int_{\gamma} f_a^{N_a}\, f_b^{N_b}\, \frac{dz}{z^{E+1}}, \quad . \quad . \quad . \quad (5)$$

where the complex integral is taken round a contour enclosing the origin $z=0$. The contour γ may be any contour lying within the circle of convergence of this power series and circulating round $z=0$ once in the counter-clockwise direction.

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[1] This presupposes that the particles are distinguishable from each other.

Let us now find out the average energy of the oscillators A. It is given by the expression

$$C\overline{E}_A = \sum_{a,\,b} \frac{(\sum r a_r\, \epsilon)\, N_a\,!\, N_b\,!}{\prod a_r\,!\, \prod b_s\,!} \,.$$

It will be easily seen that $C\overline{E}_A$ is the coefficient of z^E in the expansion of the function.

$$\left[z \frac{d}{dz}\,(1 + z^{\epsilon} + z^{2\epsilon} + \ldots\ldots)^{N_a}\right](1 + z^{\eta} + \ldots\ldots)^{N_b}$$

$$= N_a\, z \frac{d}{dz}\Big[\log f_a\Big]\, f_a^{N_a} f_b^{N_b}$$

since the extra terms $\sum r a_r \epsilon$ occurring in $C\overline{E}_A$ are obtained by the process $z \dfrac{d}{dz}$. We again use the Cauchy formula for its evaluation. We get

$$C\overline{E}_A = \frac{1}{2\pi i}\int_{\gamma} N_a\, z\, \frac{d}{dz}[\log f_a].\, f_a^{N_a}.f_b^{N_b}.\frac{dz}{z^{E+1}} \quad . \quad (6)$$

The expressions which have been deduced for C and $C\overline{E}_A$ are quite exact and hold for all values of N_a, N_b and E. Generally in physical systems these quantities are very large. We can therefore deduce the asymptotic values of these expressions for N_a and N_b tending to infinity. This can be done by the method of steepest descent.

Let us take the integrand in equation (5) on the positive real axis It tends to infinity for $z \to 0$ and $z \to 1$, and at some point between these, it passes through a unique minimum. This point is given by

$$\frac{d}{dz}\left(z^{-E} f_a^{N_a}.f_b^{N_b}\right) = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Let us denote the point so defined by ϑ. For γ take the circle of radius ϑ described with the origin as centre. From the properties of complex functions we can easily see that the modulus of the quantity to be integrated has a strong maximum at $z = \vartheta$ and decreases very rapidly as we move away from this point. Hence in finding out the integral $C\overline{E}_A$ we need consider its value only in the immediate neighbourhood of ϑ. We can therefore take the slowly variable function outside the sign of integration and write ϑ for z in it. Thus we get

$$C\overline{E}_A = \frac{1}{2\pi i} N_a\, \vartheta \frac{d}{d\vartheta} \log f_a \int_{\gamma} f_a^{N_a}.f_b^{N_b} \frac{dz}{z^{E+1}} \quad . \quad . \quad (8)$$

Using the value of C from (5) equation (8) yields

$$\overline{E}_A = N_a\, \vartheta \frac{d}{d\vartheta} \log f_a \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Let us now return to the consideration of equation (7). Introducing in this the values of f_a and f_b we obtain

$$E = \frac{N_a\,\epsilon}{\vartheta^{-\epsilon}-1} + \frac{N_b\,\eta}{\vartheta^{-\eta}-1} \qquad . \quad . \quad . \quad . \quad . \quad (10)$$

From equations (9) or (10) it will be evident that ϑ must be a function of the temperature. The exact relation can be deduced from the second law of thermodynamics or from the law of equipartition of energy. According to the latter the mean energy of a linear simple harmonic oscillator in the limit $\nu\rightarrow 0$ will be kT. Hence from (10) we have

$$kT = \frac{1}{\log 1/\vartheta}, \quad \text{or } \vartheta = e^{-1/kT}.$$

The mathematical process of limiting the integration round the neighbourhood of the minima point corresponds physically to the above-mentioned method : an isolated system having the total energy E is to be replaced by a system in contact with the thermostat T whose temperature is so chosen that the most probable energy is E.

On putting the values of ϑ and f_a in equation (9) for $\overline{E}_A$ we get

$$\overline{E}_A = \frac{N_a\,\epsilon}{e^{\epsilon/kT}-1}.$$

which is the same formula as deduced by Planck. For further applications Fowler's *Statistical Mechanics* may be consulted.

NOTE 17

Low Temperature Physics and Liquid He II

Low Temperature Physics is mainly the physics of Liq. He II, and of bodies placed in a bath of Liq. He II. A short account of the discovery of liquid He II and attempted explanation of the peculiar properties exhibited by it has been given in §12·30 and §17·10. A more detailed account is given in this Note.

As fig. 21, p. 526 shows, the phase diagram of He is quite different from that of other substances. The fusion-curve (solid-liquid phase line), and the S. V. P. curve (liquid-vapour line) do not meet in a point (Triple point) as in the case of other substances, but they are separated, as far as can be inferred now, upto absolute zero, by the liquid phase. The fusion-curve, after taking a sharp bend at the end of the λ-line proceeds almost horizontally and cuts the p-axis at $p=25$ atm. Thus even at absolute zero, liquid helium will not solidify unless an external pressure of 25 atmos. is maintained. The S. V. P. curve also appears to proceed normally to the origin ($p = 0$, $T = 0$).

Thus if external pressure is withdrawn, solid He will liquefy, and probably blow up to a gas at the A. N. This proves the existence of strong forces of repulsion amongst the atoms of He when brought close together.

The two curves are joined by the λ-line running between the points ($T = 1{\cdot}778$°K, $p = 29{\cdot}96$ atm) and ($T = 2{\cdot}186$°K, $p = {\cdot}05$ atm.) To the left, we have Liq. He II, to the right Liq. He I.

There is nothing to distinguish Liq. He I from any ordinary liquid, except that its viscosity co-efficient (when in equilibrium with its vapour) does not increase with lowering of temperature according to the formula $\eta = \eta_0 e^{A/T}$, as is the case with most liquids, but it actually decreases, as in the case of gases, according to the semi-empirical law $\eta = \eta_0 (T/T_0)^n$.

Transition to He II.

Some properties show no sudden discontinuity as the λ line is crossed. These are surface tension, vapour pressure, latent heat and dielectric constant. The specific heat, on the other hand, shows a sudden discontinuity. But discontinuities are most prominent when we study transport phenomena such as viscosity and heat conductivity or flow phenomena.

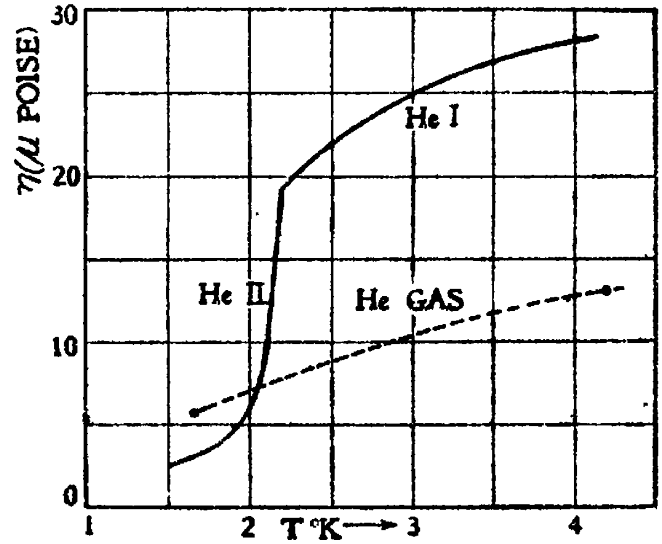

Fig. 1.—Viscosity of liquid and gaseous helium at different temperatures.

Viscosity:—The value of the viscosity coefficient of Liq. He in equilibrium with its vapour is shown in the full-line curve of Fig.[1] 1, and that of He-gas is shown by the broken curve. It is seen that there is a sharp discontinuity at the λ-point and the course of the curve on the two sides of it are different. The values of the viscosity coefficient which are plotted in Fig. 1 are obtained by the oscillating disc method[2] by Keesom and MacWood. But when attempts were made to measure viscosity by the flow through capillary method, quite different results were obtained. Below the λ-point, the flow was found to be extraordinarily large; in fact Kapitza noticed that

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[1] Taken from Tisza, *Phys. Rev.*, **72**, 838. [2] *Physica*, **5**, 737, 1938.

$$\frac{\eta \text{ for liq. He II}}{\eta \text{ for liq. He I}} \cong 10^{-3}.$$

The explanation for this striking difference in the values of viscosity as determined by these two methods is given later.

Heat Conductivity :—Heat conductivity of Liq. He I is quite normal, of the order of 10^{-4} (of the same order as for gases at ordinary temperatures), but that of Liq. He II was found to be abnormally large; in fact some observers reported that it was 800 times more conducting than even copper at room temperature and about $13{\cdot}5\times10^{8}$ times larger than that of Liq. He I, the absolute value being 820 cal/deg. cm. sec. It was found that the heat flow was not proportional to the temperature gradient. Apparently, though these experiments were designed for conductivity measurements, heat was being transported by some other mechanism.

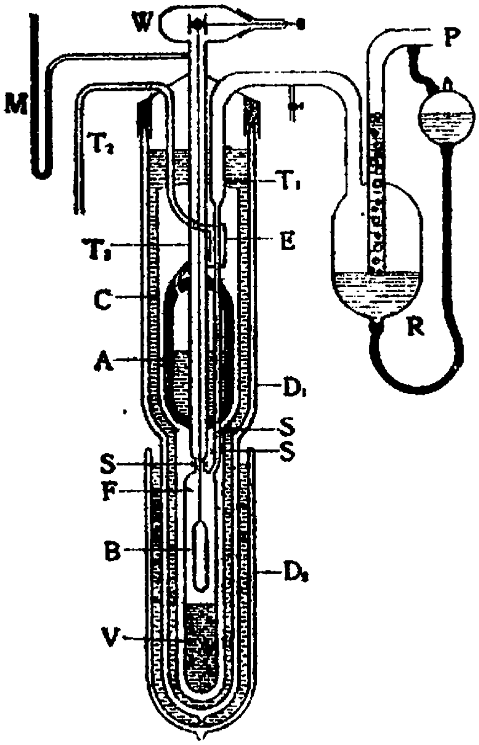

Fig. 2.—Daunt and Mendelssohn's apparatus for demonstrating the transfer effect of liq. He II.

Kapitza on the basis of his flow experiments, first postulated the hypothesis that the anomalous properties of He II were due to the formation of a "*Superfluid*" below the λ-point. Thus liquid He II is supposed to be a mixture of this superfluid and the normal fluid which is the ordinary liquid He I. The superfluid is a perfect fluid having no viscosity. Landau worked out the quantum-hydrodynamics of the superfluid, and predicted the existence of a second sound in liq. He II which was verified by Peshkov (vide infra). The second sound was predicted earlier by Tisza (1938) on the basis of London's theory of Bose-Einstein condensation. (vide supra).

The anomalous values of heat conductivity, and of liquid flow were in part traced to the formation of a creeping film of helium formed over solid surfaces generally known as the Rollin (sometimes also called Rollin-Simon) film after the authors who first suggested its existence. The properties of the film were investigated in great detail at Oxford by Daunt and Mendelssohn[1], by means of the apparatus shown in Fig. 2.

The apparatus is a liquid He-cryostat, the liquid He being contained within A and V, the outer mantles D_2 and C containing liq. N_2 and liq. H_2. As He evaporates from A, it passes through the heat exchanger E. Helium is introduced into V by the arrangement P through the heat exchanger E, and its temperature is reduced below the λ-point so that V contains Liq. He II. B is a glass beaker which can be lowered into or raised from V, by means of the arrangement W. The observations of Daunt and Mendelssohn are illustrated in Fig. 3.

(*a*) shows the beaker inside the liquid, the liquid level inside beaker being lower. In this case, liq. He creeps along the surface of the beaker in the direction shown by arrows, till the level in and out are equalized.

(*b*) shows the beaker still inside the liquid with the level of helium inside it higher. In this case, helium drains out of the beaker creeping along its surface in the direction of arrows till the level is equalised.

(*c*) shows the beaker filled with the liquid and lifted entirely out of the pool of liquid helium below. The liquid inside the beaker now drains out along the surface, and collects in the form of drops and falls into the pool of liq. He below till the whole beaker is drained out.

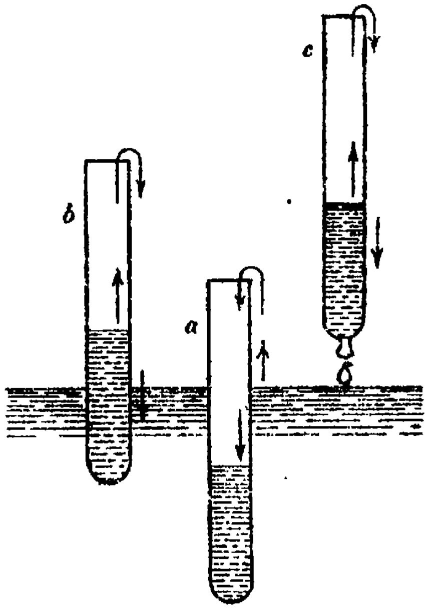

Fig. 3.—Transfer effect of liq. He II.

Liq. He II apparently seeks the lowest level, but the rate of transfer is found to be independent of the difference in level. Further the volume of the liquid which is transported in this way depends on the perimeter of the surface and the temperature but is independent of the nature of the surface. The flow can thus be expressed in $cm.^3$/cm. per sec. This highly mobile helium film is of the order of several hundred atoms thick, the film flowing over an adsorbed layer of helium atoms with a velocity of about 20 cm. per sec. below 1·5°K. This mobile property is attributed to the superfluid component of liq. He II. The abnormally high thermal conductivity of liquid He II is also attributed to this superfluid and is due to an actual transport of mass along the capillary, compensated by some kind of return flow, rather than to ordinary thermal conduction. The existence of such a flow can be directly demonstrated as explained below.

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[1] *Proc. Roy. Soc. Lond.*, **170**, 423, 439.

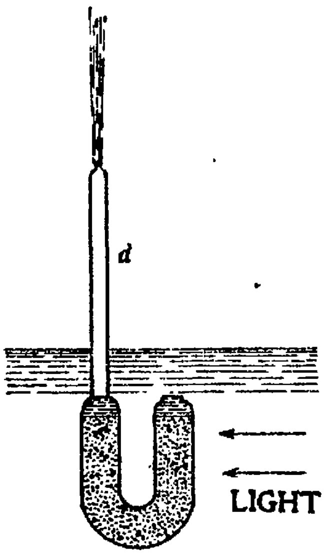

Fig. 4.—Thermohydromechanical effect of liq. He II.

Thermo-hydromechanical Effects.—

The Fountain Effect.—This phenomenon was discovered by Allen and Jones[1] at Cambridge and is illustrated in Fig. 4. *d* is a U-tube, one limb being lengthened by a capillary. It is immersed in a liq. He II bath with the capillary arm projecting out. The bent part is packed up with fine emery powder, leaving orifices of the order of 1μ between the grains. If now light from a torch is flashed on the powder, liquid He II spurts out of the capillary end, and may even rise to as great heights as 30 cm.

The Mechano-caloric Effect.—The opposite effect was discovered by Daunt and Mendelssohn[2] and is illustrated in Fig. 5. P is a Dewar flask filled partly with the same liq. He II as the bath, and provided with a constricted opening at the bottom which is plugged by fine powder. A resistance thermometer placed inside the Dewar flask and its top is closed. If the flask is now raised a few cm. above the level of the bath and the liquid allowed to drain out through the powder, the temperature inside the Dewar flask is found to rise by about 0·1°. If on the other hand, P is dipped into the bath, and the liquid is allowed to flow into it through the plug, the temperature inside the Dewar flask is found to fall.

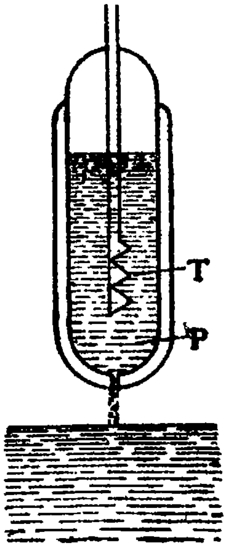

Fig. 5.—Mechano-caloric effect of liq. He II.

Both these effects have been very extensively studied by later workers.

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[1] *Nature*, **141**, 243, 1938

[2] *Nature*, **143** 719, 1939.

ATTEMPTED EXPLANATION OF THE PROPERTIES OF LIQ. He II

The extraordinary properties of Liq. He II were being found out before the outbreak of world war II. During the war, investigators in Europe and America, and in Soviet Russia began to frame theories for explaining these properties in ignorance of each other's works. Some of the assumptions and results agree, others differ. The chief investigators have been London and Tisza[1] in America and Landau in the U. S. S. R.

Most of these theories regard Liq. He II, as a mixture of two liquids, which interpenetrate each other. The one is normal liq. He I which will be described by the suffix "*n*", the other is the superfluid which will be described by the suffix "*s*". The density of the liquid is given by $\rho=\rho_n+\rho_s$ where ρ_n is the density of the normal liquid, ρ_s that of the superfluid.

The superfluid is taken to consist of He-atoms with zero energy, and zero entropy. It begins to be formed at the λ-point, but its proportion goes on increasing as the temperature is lowered till at the absolute zero, the whole mass becomes superfluid. It is assumed that the atoms of the superfluid do not interchange momentum with atoms of the normal fluid or with the surface of the containing vessel.

Landau[2] draws the follwing picture :—

At absolute zero, liq. He is a liquid without thermal motion. As temperature is increased, thermal agitation begins to appear, not continuously but as quanta, which may be called "*Phonons*" or quanta of sound, and *rotons*, which are described as elementary excitations of the vortex spectrum. These quanta behave like gases and interchange energy with walls. But as definite quantities of energy are required to produce either type of quanta, energy of translatory motion cannot change into quanta, until the velocity of flow exceeds a certain limit. Kapitza claims to have found that this critical velocity is about a metre per sec.

These assumptions go a long way in explaining the anomalous results on flow through tubes, flow through capillaries, and anomalous results on viscosity. When liq. He II flows through a tube, it is only the normal liq. He which is subjected to the laws of viscous flow, for the superfluid has $\eta=0$, and its flow is not subject to Poisseuille's law. Therefore when Liq. He II flows through a narrow capillary or through fine powder, it is only the superfluid which passes, the normal liquid is held stationary by the walls; there is therefore no gradient in the velocity of the normal fluid, and hence no viscous effects are observed i.e. the viscosity becomes vanishingly small.

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[1] *Phys. Rev.*, **72**, 838, 1947.

[2] For full details see *Phys. Rev.*, **75**, 884, 1949.

The Viscosity Experiments :

When viscosity is determined by observing the damping of a torsion pendulum, it is only the atoms of normal He which interchange energy with the moving parts. The atoms of the superfluid do not interchange any energy. Similarly when we determine the moment of inertia of liquid He II by observing the period of vibration, what we determine is the quantity due to the normal component, for only the normal fluid is dragged along by the discs on account of viscous forces, the superfluid remaining stationary. Let the quantity measured experimentally be I, and that obtained from geometry be I_0. We have then $I = I_0 \rho_n/\rho$.

This conception has been used by Andronikashvili[1] in Kapitza's laboratory to find out the ratio ρ_n/ρ. In his experiments the rotating system consisted of a set of parallel and equi-distant aluminium discs (separation distance 0·21 mm.) fixed on a common axis. This system of plates was suspended in liquid He II by a fine torsion fibre and the period of torsional oscillations observed from which I and hence ρ_n was calculated. The results are shown in Fig. 6. This constitutes the most direct method of calculating ρ_n. By observing the logarithmic decrement of the oscillation the product $\eta_n \rho_n$ could be calculated, from which the viscosity η_n of the normal fluid is determined.

Thermo-Hydrodynamics of Liq. He II.

A mathematical expression for the Fountain Effect and the Mechano-caloric effect can be deduced with the aid of the above ideas.

Let us take a cylindrical Dewar flask, plugged in the middle by emery powder, just as in the porous plug experiment (p. 504). Both sides are filled with liq. He II, at the temperatures T_A and T_B and they are closed with pistons exerting the pressures p_A and p_B. Let us now allow the piston A to move forward, and drive one mol of liq. He II, through the plug to B, the piston on the other side also moving so that the pressure p_B is maintained. The work done on the liquid to the left hand side is $p_A V_A$, and the work done by the liquid on the right side is $p_B V_B$. Now as the liquid passing through the capillary has zero entropy, and this dilutes the liquid in B with more superfluid He, the specific entropy in B is diminished and correspondingly that in A is increased. For the transfer of such a fluid for which entropy is zero, the second law of thermodynamics $dW = -dU + TdS$ gives, by the addition of the relation $S\,dT = 0$, the equation

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[1] *J. Exptl. Theoret. Phys.* U.S.S.R **16**, 780, 1946. See also Hollis-Hallett, *Proc. Roy. Soc. London*, **210**, 404, 1952.

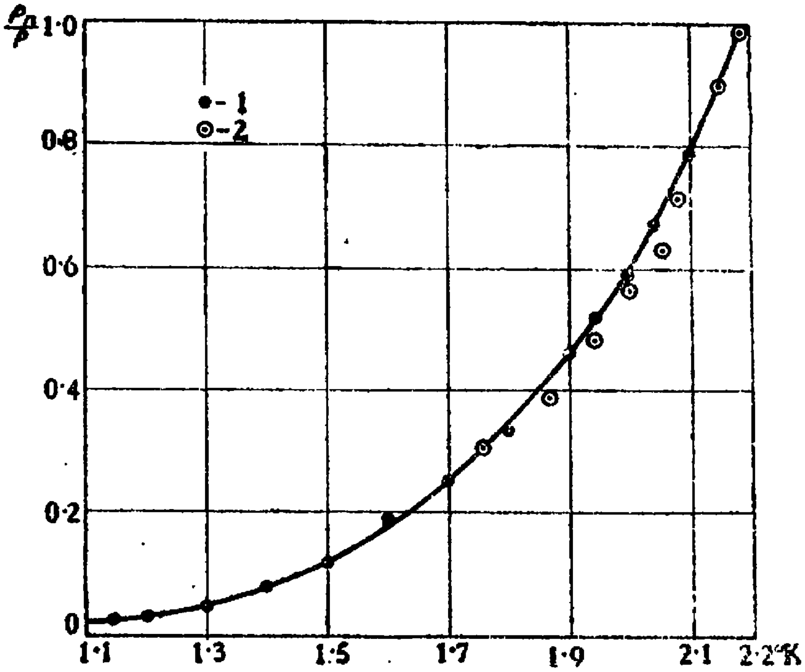

Fig. 6.—Proportion of the normal component at different temperatures.

$$dW = -d(U-TS) = -dF,$$

or

$$p_B V_B - p_A V_A = F_A - F_B, \quad . \quad . \quad . \quad . \quad (1)$$

where F_A and F_B are the free energies in A and B. We have therefore

$$U_A + p_A V_A - T_A S_A = U_B + p_B V_B - T_B S_B. \quad . \quad . \quad . \quad (2)$$

or

$$G_A = G_B,$$

i.e. the Gibbs' function remains unchanged in the process. We have as proved on p. 348,

$$dG = V.dp - S\,dT = 0 \text{ from (2).}$$

Hence

$$\frac{\Delta p}{\Delta T} = S/V = \rho s \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This relation was first deduced by H. London[1], and has been verified experimentally by Kapitza[2] and later by Mellink and Meyer.[3] The results are shown in fig. 7. The abscissa represents temperatures, the ordinate the value of $\triangle p$ as indicated by the height to which

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[1] *Nature, London*, **142**, 612, 1938; *Proc. Roy. Soc.*, **171**, 484, 1939.

[2] *J. Phys. U. S. S. R.*, **4**, 181, 1941. [3] *Physica*, **13**, 197, 1947.

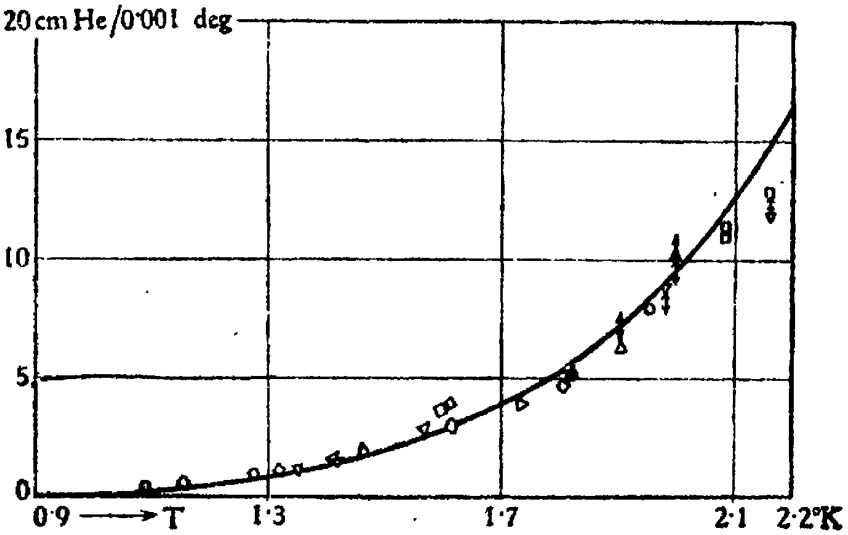

Fig. 7.—Thermo-hydromechanical effect at different temperatures.

liq. He II rises for a temperature change of 10^{-3} calculated from the relation (3), viz.

$$\triangle p = \rho s \triangle T = \rho g h,$$

$$\therefore \qquad h = s \,.\, \triangle T/g. \qquad \ldots\ldots \qquad (4)$$

$\triangle T$ is taken to be $\cong 10^{-3}$.

Table 1.—Specific Heat and Entropy of Liq. He II at different temperatures.

T °K	c_v cal./gm. deg.	s cal./gm. deg.	ρ_n/ρ
2·186	2·85	·390	1
2·18	2·05	·3701	
2·15	1·66	·3383	·860
2·10	1·41	·2951	·738
2·05	1·218	·2583	·641
2·0	·918	·2260	·552
1·9	·691	·1714	·420
1·8	·525	·1278	·307
1·7	·391	·09324	·222
1·6	·269	·06582	·157
1·5	·176	·04477	·104
1·4	·116	·02964	·067
1·3	·0705	·01892	·042
1·2	·0411	·01160	·025
1·1		·00684	·0143

The values of the relevant quantities have been taken from Table 1 reproduced partly from one by Band and Meyer, *Phys. Rev.* **74**, p. 388.

The effect is found to be independent of the width of the capillary below a certain limit, which depends on the temperature. The critical velocity at which the first *relaxation* between temperature effect and fountain effect occurs was found to be 30-40 cm/sec. at 1·3°K, decreasing to 4 cm./sec. at. 2·1°K. For further information, see papers by Band and Meyer, *loc. cit.*

Propagation of Sound Wave in Liq. He II: Velocities of First and Second Sound.

Before taking up this topic, let us recapitulate the methods of finding out the expression for velocity of sound in a liquid. Let us suppose that the sound is propagated along the x-axis and the displacement due to sound wave at a point x be ξ, which is a small quantity of the first order. Let us now take the small element of volume dx bounded by the points x, and $x+dx$, and having unit cross section; the kinetic energy per unit volume due to sound waves is $\frac{1}{2}\rho\dot{\xi}^2$. Now let us calculate the potential energy of compression per unit volume. This is obtained by considering the variation of internal energy u in the element of volume $dx = v$.' Let us denote variations due to passage of sound wave by the symbol Δ. Then we have for the volume v

$$\Delta u = \frac{\partial u}{\partial v}\,\Delta u + \frac{\partial u}{\partial s}\Delta s + \frac{1}{2}\left\{\frac{\partial^2 u}{\partial v^2}\,\Delta v^2 + 2\,\frac{\partial^2 u}{\partial v \partial s}\,\Delta v.\Delta s + \frac{\partial^2 u}{\partial s^2}\,\Delta s^2\right\} \quad (5)$$

where v and s are the specific volume and specific entropy of the liquid.

Now from the relation $du + pdv = Tds$,

$$(\partial u/\partial v)_T = -p, \quad (\partial u/\partial s)_v = T. \quad . \quad . \quad . \quad (6)$$

Hence (5) yields

$$\Delta u + p\Delta v - T\Delta s = \frac{1}{2}\left\{\frac{\partial^2 u}{\partial v^2}\,\Delta v^2 + 2\,\frac{\partial^2 u}{\partial v \partial s}\,\Delta v.\Delta s + \frac{\partial^2 u}{\partial s^2}\,\Delta s^2\right\}$$

Now $\Delta u + p\Delta v - T\Delta s$ may be put equal to the potential energy due to the sound wave for the volume v under consideration; for Δu is the change in internal energy, $p\Delta v$ is the work done on the volume v. From this, we have to deduct $T\Delta s$, which is the amount dissipated in heat production. Hence we have

W = potential energy per unit vol. = $(\Delta u + p\Delta v - Tds)/v$

$$= \frac{1}{2v}\left(\frac{\partial^2 u}{\partial v^2}\Delta v^2 + 2\,\frac{\partial^2 u}{\partial v\partial s}\Delta v.\Delta s + \frac{\partial^2 u}{\partial s^2}\Delta s^2\right) \quad . \quad (7)$$

Let us now find out Δv and Δs. Δv is the expansion caused to the slab $dx = v$ by the passage of sound waves. Now the point x is shifted to $x+\xi$, and $x+dx$ to $x + dx + \xi + (\partial\xi/\partial x)\,dx$. Hence the elongation of the slab dx is $(\partial\xi/\partial x)\,dx$ and $\Delta v = (\partial\xi/\partial x)\,dx$, or since $dx = v$, we have $\Delta v/v = \partial\xi/\partial x$.

In the usual sound propagation Δs is taken to be zero, but we cannot do so here. However if in the first instance Δs were to be put $= 0$ we have

$$W = \frac{1}{2v}\,\frac{\partial^2 u}{\partial v^2}\Delta v^2 = \tfrac{1}{2}\left(-v\,\frac{\partial p}{\partial v}\right)_s\left(\frac{\Delta v}{v}\right)^2 . \quad . \quad . \quad (8)$$

Now $-v.\,\partial p/\partial v = E_s$, the coefficient of adiabatic elasticity. Hence we have $W = \frac{1}{2}E_s.(\partial\xi/\partial x)^2$, and the kinetic energy $L = \frac{1}{2}\rho\dot{\xi}^2$. Using the Lagrangian form of equation of motion $\frac{d}{dt}\left(\frac{\partial L}{\partial\dot{\xi}}\right) - \frac{d}{dx}\left(\frac{\partial W}{\partial\xi_x}\right) = 0$, we obtain $\rho\ddot{\xi} = E_s\frac{\partial^2\xi}{\partial x^2}$ as the equation for wave-propagation. From this the velocity of propagation $\mathcal{V}$ is seen to be equal to $\sqrt{E_s/\rho}$.*

Let us now find out expressions for kinetic energy and potential energy per unit volume in the present case, where $\Delta s \neq 0$.

The kinetic energy per unit volume is given by

$$L = \tfrac{1}{2}\rho_n.\,\dot{\xi}_n^2 + \tfrac{1}{2}\rho_s.\,\dot{\xi}_s^2 \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where ξ_n = displacement of normal fluid, ξ_s that of superfluid. Further as before, we have

$$\frac{\Delta\rho_n}{\rho_n} = -\frac{\Delta v_n}{v_n} = -\frac{\partial\xi_n}{\partial x},\quad \frac{\Delta\rho_s}{\rho_s} = -\frac{\partial\xi_s}{\partial x}, \quad . \quad . \quad . \quad (10)$$

from which we deduce that

$$\frac{\Delta\rho}{\rho} = \frac{\Delta(\rho_n+\rho_s)}{\rho} = \frac{\Delta\rho_n}{\rho_n}\,\frac{\rho_n}{\rho} + \frac{\Delta\rho_s}{\rho_s}\,\frac{\rho_s}{\rho} = -\frac{\partial}{\partial x}\left(\frac{\xi_n\rho_n+\xi_s\rho_s}{\rho}\right)$$

$$= -\frac{\partial\xi_1}{\partial x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

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*$\xi_x \equiv \partial\xi/\partial x$. For details, see Courant and Hilbert, Methoden etc., vol. 1, Chap. IV.

from (10), where $\xi_1 = (\xi_n\rho_n+\xi_s\rho_s)/\rho$. ξ_1 is a new co-ordinate, which denotes the displacement of the centre of gravity of the whole mass.

(*N. B.*—Note that we take $\frac{\partial(\rho_n/\rho)}{\partial x} = 0$, $\frac{\partial(\rho_s/\rho)}{\partial x} = 0$. The proportions of the normal fluid and superfluid are thus assumed to be unaltered by the passage of sound waves which is a reasonable assumption.)

The entropy variation $\triangle s$ of the element dx is obtained from the following considerations. We have

$$\rho s = \rho_n s_n + \rho_s s_s.$$

Here s is the average entropy per unit mass, s_n that of normal fluid, s_s that of the superfluid. Let us take $s_s = 0$. Then $\rho s = \rho_n s_n$.

Or
$$\frac{\triangle s}{s} + \frac{\triangle \rho}{\rho} = \frac{\triangle \rho_n}{\rho_n} + \frac{\triangle s_n}{s_n},$$

the symbol $\triangle$ denoting variation due to passage of sound waves. Now since n denotes a normal fluid, *we may put* $\triangle s_n = 0$, *as in all acoustic propagations through normal fluids, entropy does not change.* Hence

$$\frac{\triangle s}{s} = \frac{\triangle \rho_n}{\rho_n} - \frac{\triangle \rho}{\rho} = -\frac{\partial}{\partial x}\frac{[\rho_s(\xi_n - \xi_s)]}{\rho} = -\frac{\partial \xi_2}{\partial x} \quad . \quad . \quad (11a)$$

We introduce thus a second variable ξ_2 given by $\xi_2 = \frac{\rho_s}{\rho} . (\xi_n - \xi_s)$.

It can be shown from (9) by simple substitution that in terms of the new variables ξ_1, ξ_2 we have

$$L = \tfrac{1}{2}\rho\,[\dot{\xi}_1^2 + (\rho_n/\rho_s)\dot{\xi}_2^2] \quad . \quad . \quad . \quad . \quad . \quad (12)$$

since
$$\xi_n = \xi_1 + \xi_2, \quad \xi_s = \xi_1 - (\rho_n/\rho_s)\xi_2.$$

Let us find out the value of the potential energy. We have as before

$$\tfrac{1}{2}\,\frac{1}{v}\,\frac{\partial^2 u}{\partial v^2}\Delta v^2 = \tfrac{1}{2}E_s\left(\frac{\partial \xi_1}{\partial x}\right)^2,$$

and from (6) and (11a) the third term in (7) is

$$\frac{1}{2v}\,\frac{\partial^2 u}{\partial s^2}\triangle s^2 = \tfrac{1}{2}\rho s^2\left(\frac{\partial T}{\partial s}\right)_v\left(\frac{\triangle s}{s}\right)^2 = (\rho s^2 T/c_v)\left(\frac{\partial \xi_2}{\partial x}\right)^2.$$

It can be shown that

$$\frac{\partial^2 u}{\partial v\,\partial s} = -\alpha . E_T . T/c_v.$$

$$\Bigg[\ \text{Proof:—We have } \left(\frac{\partial u}{\partial v}\right)_s = -p,\quad \frac{\partial^2 u}{\partial v \partial s} = -\left(\frac{\partial p}{\partial s}\right)_v = \left(\frac{\partial T}{\partial v}\right)_s$$

by thermodynamical relations. To find out $\left(\frac{\partial T}{\partial v}\right)_s$, we take $s = f(T, v)$; then it can be easily shown that

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial s}{\partial v}\right)_T \Big/ \left(\frac{\partial s}{\partial T}\right)_v = -\left(\frac{\partial p}{\partial T}\right)_v \Big/ \left(\frac{\partial s}{\partial T}\right)_v$$

$$\text{Now} \quad \left(\frac{\partial p}{\partial T}\right)_v = \left(-v\frac{\partial p}{\partial v}\right)_T \cdot \left(\frac{1}{v}\cdot\frac{\partial v}{\partial T}\right)_p = \alpha E_T,$$

$$\text{and} \qquad \left(\frac{\partial T}{\partial s}\right)_v = T/c_v; \quad \text{hence } \frac{\partial^2 u}{\partial v \partial s} = -\alpha E_T T/c_v, \Bigg]$$

$$\triangle v = v.\ \partial\xi_1/\partial x, \quad \triangle s = -s\partial\xi_2/\partial x.$$

We have therefore for potential energy per unit volume,

$$W = \tfrac{1}{2}\left[E_s\left(\frac{\partial \xi_1}{\partial x}\right)^2 + \frac{2\alpha\, E_T\,.\,Ts}{c_v}\cdot\frac{\partial \xi_1}{\partial x}\cdot\frac{\partial \xi_2}{\partial x} + (\rho s^2 T/c_v)\left(\frac{\partial \xi_2}{\partial x}\right)^2\right] \qquad (13)$$

Further, as already proved above, the equations of motion are easily seen to be given by

$$\rho\ddot{\xi}_1 = E_s\frac{\partial^2\xi_1}{\partial x^2} + \frac{\alpha E_T\,.\,Ts}{c_v}\frac{\partial^2\xi_2}{\partial x^2},$$

$$\frac{\rho\,\rho_n}{\rho_s}\ddot{\xi}_2 = \frac{\alpha E_T\,.\,Ts}{c_v}\cdot\frac{\partial^2\xi_1}{\partial x^2} + \frac{\rho s^2 T}{c_v}\frac{\partial^2\xi_2}{\partial x^2}.$$

The coefficient of thermal expansion is very small for He II ($\alpha \sim -3\times10^{-3}$ deg.$^{-1}$). Therefore if, as a first approximation, we neglect the coupling terms, the equations reduce to

$$\rho\ddot{\xi}_1 = E_s\,.\,\frac{\partial^2\xi_1}{\partial x^2}$$

for the equation of ordinary sound propagation, and

$$\frac{\rho_n}{\rho_s}\ddot{\xi}_2 = \frac{s^2 T}{c_v}\frac{\partial^2\xi_2}{\partial x^2}$$

for equation of propagation of second sound. We have therefore, the velocity of ordinary sound $\mathcal{V}_1^2 = E_s/\rho$, and the velocity of the second sound $\mathcal{V}_2^2 = \frac{s^2 T}{c_v}\,.\,\frac{\rho_s}{\rho_n}$.

The physical interpretation of the two results is now apparent. The vector $\xi_1 = (\rho_s\xi_s + \rho_n\xi_n)/\rho$ denotes the displacement of the centre of mass, the normal fluid and the superfluid moving together during this displacement. Since $\partial\xi_1/\partial x = -\triangle\rho/\rho$, this displacement causes density fluctuations and pressure waves as in ordinary sound. The equation therefore represents ordinary sound waves propagated with the velocity given by the usual expression $\mathcal{V}_1 = \sqrt{E_i/\rho}$. The vector $\xi_2 = \rho_s(\xi_n - \xi_s)/\rho$ denotes relative displacement of the normal fluid with respect to the super-fluid, and as it satisfies the relation $\partial\xi_2/\partial x = -\Delta s/s$, its variation denotes entropy fluctuations. Now entropy fluctuations will cause fluctuations of temperature, hence the second equation represents propagation of temperature waves. The velocity $\mathcal{V}_2$ is given by $\mathcal{V}_2 = \sqrt{Ts^2\rho_s/\rho_n c_v}$. We can find out expressions for the velocity of the two waves from the data given in Table 1. At $T = 1{\cdot}3$°K, $\mathcal{V}_1$ comes out to be 230 metres/sec. This does not much vary with temperature. As regards the second wave its velocity behaves in a more complicated way. At the λ-point (and above), $\mathcal{V}_2 = 0$ to start with. Then it begins to grow, but for its calculation, we must have a knowledge of s, c_v, ρ_s and ρ_n. Using the data given in Table 1, we find $\mathcal{V}_2$ to be about 25 metres at 1·33 °K.

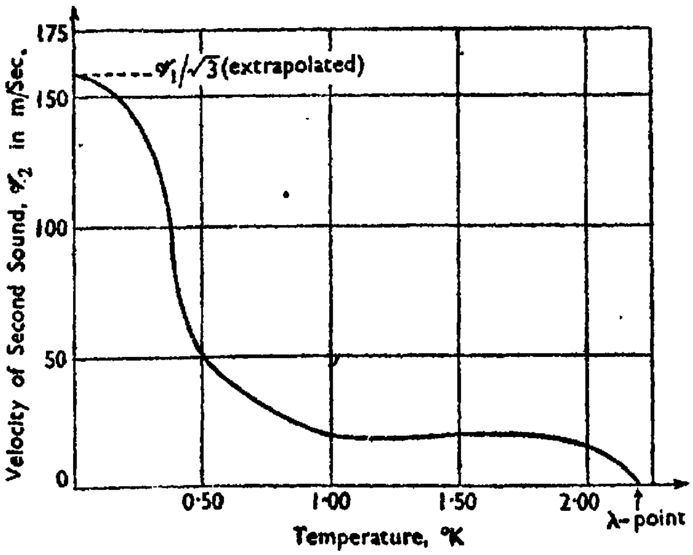

Fig. 8.—Velocity of second sound as a function of temperature. (*Peshkov, Maurer and Herlin, Atkins and Osborne.*)

The existence of the second wave was first predicted by Tisza.[1] and independently by Landau[2]. As their theories differ in details, the variation of velocity of the second sound with temperature as given by them is different. According to Tisza's theory the velocity should not vary much below 1·6°K but according to Landau it should increase below 1·1°K, reaching the limiting value $\mathcal{V}_1/\sqrt{3} = 137$ m./sec. at the absolute zero.

The experimental verification of the theory of the second wave was first obtained by Peshkov[3] working in Kapitza's laboratory in Moscow.

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[1] *C. R. Acad. Sci. Paris*, **207**, 1035, 1938; *J. phys. radium*, **8**, 164, 1940; *Phys., Rev.*, **72**, 838, 1947.

[2] *J. Phys. U. S. S. R*, **5**, 71, 1941.

[3] *J. Exp. Theo. Phys. U. S. S. R.* **10**, 389, 1946.

Peshkov first showed the increase of second-sound velocity with temperature below 1·1°K, which supports Landau's theory. Peshkov set up standing second sound waves in a cylindrical column of liquid He II between two flat discs wound with resistance wires. An alternating electric current served to produce temperature fluctuations in one disc and the other disc was moved from temperature maximum to temperature minimum to detect the nodes and antinodes. Pellam used pulsed heat from a multivibrator from which he could measure both the velocity and the attenuation of the second sound. Pellam and Scott found that the second sound velocity rises to 33·9 m./sec. at a still lower temperature while Atkins and Osborne[1] find for the velocity at 0·1°K the value 152 m./sec. These results are shown in Fig. 8. For fuller information regarding the present state of the theory of liquid helium, see *Advances in Physics* Vol. 1, pp. 111—209, 1952, or Gorter, *Progress in low temperature Physics* (1955) Vols I and II.

NOTE 18

Thermal Diffusion

1. Elementary theory of thermal diffusion.—The phenomena of thermal diffusion has been briefly described in § 3·42. We shall first give here a simple theoretical treatment of the phenomenon following the method of Fürth who has extended the simple mean free path treatment assuming maxwellian distribution to this case also.

It is obvious that the treatment of pure diffusion given in §3·40 must be modified in this case to include the temperature gradient and hence change of $\bar{c}_1$ and $\bar{c}_2$ with z also. In place of equation (83) p. 177 we shall now have for the number ν_1 of molecules of the first type crossing unit area in unit time the relation

$$\nu_1 = \int_0^\infty \int_0^\pi \left[A_1 - a(z_0 - \lambda_c \cos\theta)\right] \tfrac{1}{2} \sin\theta \cos\theta \, d\theta. \left[c(z_0) - \lambda_c \cos\theta \frac{d\bar{c}}{dz}\right] \times f(c)dc$$

$$= \tfrac{1}{3} a \int_0^\infty c\lambda_c f(c)dc - \tfrac{1}{3}\int_0^\infty \frac{d\bar{c}}{dz}\, n_1 \lambda_c f(c)\, dc,$$

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[1] *Phil. Mag.*, **41**, 1078, 1950.

neglecting terms containing products of a and $d\bar{c}/dz$ and putting $n_1 = A_1 - az_0$, the concentration at the plane z_0. Putting $a = -dn/dz$ we have

$$\nu_1 = -\tfrac{1}{3}\left[\frac{dn_1}{dz}\bar{c}_1\lambda_1 + \frac{d\bar{c}_1}{dz}n_1\lambda_1'\right] \quad . \quad . \quad . \quad (1)$$

We have introduced λ_1 and λ_1' as the two mean free paths defined in different ways. Similarly,

$$\nu_2 = -\tfrac{1}{3}\left[\frac{dn_2}{dz}\bar{c}_2\lambda_2 + \frac{d\bar{c}_2}{dz}n_2\lambda_2'\right]$$

As explained on p. 178 the resultant transfer $\nu_1+\nu_2$ has to be annulled by a mass velocity w such that $w = -(\nu_1-\nu_2)/(n_1+n_2)$ and the true flux of molecules (1) is $\Gamma_1 = (\nu_1 n_2 + \nu_2 n_1)/(n_1+n_2)$. The mean velocity of flux of molecules (1) is $\bar{w}_1 = \Gamma_1/n_1$ and for molecules (2), $\bar{w}_2 = \Gamma_2/n_2$. The diffusion velocity is

$$\bar{w}_1 - \bar{w}_2 = \frac{\Gamma_1}{n_1} - \frac{\Gamma_2}{n_2}$$

$$= -\tfrac{1}{3}\left[\frac{1}{n_1}\frac{dn_1}{dz}\bar{c}_1\lambda_1 - \frac{1}{n_2}\frac{dn_2}{dz}\bar{c}_2\lambda_2 + \lambda_1'\frac{d\bar{c}_1}{dz} - \lambda_2'\frac{d\bar{c}_2}{dz}\right] \quad . \quad (2)$$

Since the partial pressure of molecules (1) is

$$n_{10}p = n_1 kT, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where p is the total pressure equal to $(n_1+n_2)kT$ and n_{10} is the fractional concentration $n_1/(n_1+n_2) = n_1/n$, we have

$$\frac{dn_1}{dz} = \frac{p}{k}\left[\frac{1}{T}\frac{dn_{10}}{dz} - \frac{n_{10}}{T^2}\frac{dT}{dz}\right]$$

or

$$\frac{1}{n_1}\frac{dn_1}{dz} = \frac{1}{n_{10}}\frac{dn_{10}}{dz} - \frac{1}{T}\frac{dT}{dz}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Again, since $\bar{c} = \sqrt{(8kT/m\pi)}$,

$$\frac{d\bar{c}_1}{dz} = \left(\frac{8k}{m\pi}\right)^{1/2}\frac{1}{2}\frac{1}{T^{1/2}}\frac{dT}{dz} \quad . \quad . \quad . \quad . \quad (5)$$

Hence equation (2), using (4) and (5) yields

$$\bar{w}_1 - \bar{w}_2 = -\frac{1}{3}\left[\bar{c}_1\lambda_1\frac{1}{n_{10}}\frac{dn_{10}}{dz} - \bar{c}_2\lambda_2\frac{1}{n_{20}}\frac{dn_{20}}{dz} - \frac{1}{T}\frac{dT}{dz}(\bar{c}_1\lambda_1 - \bar{c}_2\lambda_2)\right.$$
$$\left. + \frac{1}{2}\left(\frac{8k}{\pi T}\right)^{1/2}\frac{dT}{dz}\left(\frac{\lambda_1'}{m_1^{1/2}} - \frac{\lambda_2'}{m_2^{1/2}}\right)\right] \quad . \quad . \quad . \quad (6)$$

---

[1] $\bar{w}_1$ and $\bar{w}_2$ represent the mean molecular velocities in the z-direction and would be zero if the gas were in equilibrium state (i.e. uniform n and T).

where the first two terms give the pure diffusion, and as shown on p. 182, will yield, since $dn_{10}/dz = -dn_{20}/dz$, and $\Gamma_1/n_1 - \Gamma_2/n_2 = \Gamma_1\,(n_1+n_2)/n_1n_2$,

$$D_{12} = \frac{1}{3} n_{10}\, n_{20} \left(\frac{\lambda_1 \bar{v}_1}{n_{10}} + \frac{\lambda_2 \bar{v}_2}{n_{20}} \right)$$

$$= \frac{1}{3} n_{10}\, n_{20} \left(\frac{8kT}{m_1 m_2 \pi} \right)^{1/2} \left[\frac{\lambda_1 \sqrt{m_2}}{n_{10}} - \frac{\lambda_2 \sqrt{m_1}}{n_{20}} \right] \quad . \quad . \quad (7)$$

Therefore equation (6) can be written in the form

$$\bar{w}_1 - \bar{w}_2 = - \frac{1}{n_{10}\, n_{20}} \left[D_{12} \frac{dn_{10}}{dz} + \frac{D_T}{T} \frac{dT}{dz} \right], \quad . \quad . \quad . \quad (8)$$

where

$$D_T = - \frac{1}{3} n_{10}\, n_{20} \left(\frac{8kT}{m_1 m_2 \pi} \right)^{1/2} \left[\left(\lambda_1 - \frac{\lambda_1}{2} \right) \sqrt{m_2} - \left(\lambda_2 - \frac{\lambda_2'}{2} \right) \sqrt{m_1} \right]$$

Thus we can write

$$D_T = D_{12}\, k_T \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where
$$k_T = \frac{(\lambda_2 - \lambda_2'/2)\sqrt{m_1} - (\lambda_1 - \lambda_1'/2)\sqrt{m_2}}{n_{10}\, \lambda_2 \sqrt{m_1} + n_{20}\, \lambda_1 \sqrt{m_2}}\, n_{10}\, n_{20} \quad . \quad . \quad (10)$$

It is usual to put $k_T/n_{10}\, n_{20} = \alpha$. The quantities D_T, k_T and α are respectively called *thermal diffusion coefficient*, *thermal diffusion ratio* and *thermal diffusion factor.*

The transfer rate of number of molecules of type (I), which by convention is taken to be the heavier component, is

$$\Gamma_1 = -(n_1 + n_2) \left[D_{12} \frac{dn_{10}}{dz} + \frac{D_T}{T} \frac{dT}{dz} \right]. \quad . \quad . \quad . \quad (11)$$

and the net transfer of mass is $S = \Gamma_1(m_1 - m_2)$.

The steady state is characterised by any of the conditions: $\bar{w}_1 = 0$, $\bar{w}_2 = 0$, $\Gamma_1 = 0$, $S = 0$. Hence when the steady state is attained after lapse of sufficient time, the concentration gradient is given by

$$\frac{dn_{10}}{dz} = - k_T \frac{1}{T} \frac{dT}{dz}\,, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

which shows that for positive values of k_T or α the heavier gas (1) gets concentrated in the colder bulb.

2. Values of α :

The expression for k_T or α is seen from (10) tobe a complicated function of the masses, concentrations and the mean free path (i.e. molecular diameter also). For comparison with experimental results the exact expressions for α given by Chapman and Enskog[1] must be utilised which is however, very complicated and involves the laws of interaction between like and unlike molecules viz. those between (1, 1), (2, 2) and (1, 2). The expression simplifies considerably if (a) the colliding molecules can be regarded as rigid elastic spheres, or (b) they repel each other with a force $F = Kr^{-s}$. The value of α for a mixture of heavy isotopes in the first case is approximately given by

$$\alpha_\infty = \frac{105}{118}\cdot\frac{m_1-m_2}{m_1+m_2} = 0{\cdot}89.\frac{m_1-m_2}{m_1+m_2}. \quad . \quad . \quad (13)$$

In the second case it is given by

$$\alpha = \alpha_\infty \frac{s-5}{s-1}C(s), \quad . \quad . \quad . \quad . \quad (13a)$$

where $C(s)$ is a complex function of s, which has been calculated from $s = 3$ to $s = \infty$. The value $s = \infty$, corresponds to the assumption of rigid elastic spheres. The values of $C(s)$ are given in table 1.

Table 1.—*Values of* $C(s)$.

s	3	4	5	6	7	8	9	10	11	12	13	14	15	∞
$C(s)$	·807	·809	·816	·828	·843	·854	·865	·874	·882	·890	·896	·901	·906	1

For $s = 5$, $\alpha(s) = 0$. If $s > 5$, α is positive; for $s < 5$, α is negative.

As explained on p. 171, s can be obtained if we have a range of values of viscosity coefficient η, which is found to obey the law $\eta/\eta_0 = (T/T_0)^n$. We have then $s = (2n+1)/(2n-1)$. Experiments however show that n does not remain constant over a large range of temperatures.

These values of α are however only approximate. Further this method of deducing the value of s is applicable only when all molecules are of the same chemical type as in a mixture of isotopes. When we have a mixture of two different species of gases say N_2 and O_2, the force of repulsion may be supposed to be given by $F \propto r^{-s_{12}}$, the force between molecules of the same type being given by $F \propto r^{-s_{11}}$, $r^{-s_{22}}$. While s_{11}, s_{22}, can be obtained as explained above, s_{12} has to be obtained from temperature variation of the interdiffusion constant. Such values have been given by Chapman, from measurements by Ibbs and his coworkers.

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[1] See Chapman and Cowling, *Mathematical theory of non-uniform gases*, Chapter XIV.

3. Experimental Test of Thermo-diffusion—After the first experimental verification of (11) by Chapman and Dootson in 1917, numerous experiments have been carried out by Ibbs, Grew and their co-workers in England, by Nier and others in the U. S. A. and by Blüh and Blüh in Germany, by Itterbeck, Paemela and others in Holland using mixtures of gases. In all these experiments, two vessels, connected by a narrow tube, are filled up with the known mixture and then the vessels are placed in baths maintained at fixed but different temperatures. A temperature gradient sets in along the connecting tube and diffusion takes place according to (8). Finally, after sufficient time has elapsed, a steady state is reached given by (12). The equilibrium concentration is found by integrating (12) if we treat k_T as constant. We get

$$n_{10}-n_{10}' = k_T \ln T'/T. \quad . \quad . \quad . \quad . \quad (14)$$

where T, T' are the temperatures of the two bulbs, n_{10}, n_{10}' the respective concentrations in the steady state; $n_{10}-n_{10}'$ is called the separation.

Since, however, k_T is strongly dependent upon n_{10}, it is preferable to use α instead of k_T. Equation (12) then becomes

$$\frac{1}{n_{10}n_{20}}\,\frac{dn_{10}}{dz} = -\alpha\frac{1}{T}\,\frac{dT}{dz},$$

or

$$dn_{10}\left[\frac{1}{n_{10}}+\frac{1}{1-n_{10}}\right] = -\frac{\alpha}{T}\,dT.$$

Hence

$$\left(\frac{n_{10}}{n_{20}}\right)\Big|\left(\frac{n_{10}'}{n_{20}'}\right) = \left(\frac{T'}{T}\right)^{\alpha}. \quad . \quad . \quad . \quad . \quad (15)$$

The left-hand side of equation (15) is called the *separation factor q* and is the quantity usually measured experimentally. We have therefore

$$\alpha = \frac{\log q}{\log (T'/T)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

It is usually but not always, the practice to choose one of the vessels rather large compared with the other. The value of n_{10} for the smaller vessel alone is measured by different methods. Ibbs and his co-workers measure the change in concentration by measurement of thermal conductivity, Nier from mass spectroscopic analysis, Itterbeck and his coworkers by the change in viscosity, Blüh and Blüh by change in the refractive index. A typical apparatus due to Grew is described below :

The apparatus used by K. E. Grew for measurements of thermal diffusion in gas mixtures consisted of a diffusion vessel A-B of the shape shown in Fig. 1. The upper part A of this vessel could be maintained at any desired temperature up to 450°C by placing it inside an electric furnace carefully designed to secure uniformity of temperature within 2°C. The lower part B between the stopcocks T_1 and T_2 was immersed in a water thermostat maintained at 20°C. The temperature of A was measured by a chromel-alumel thermocouple Th placed close to the bulb A. The volumes of A and B were 20 c.c. and 2·5 c.c. respectively. For measurements at low temperatures the vessel was inverted and the part A immersed in a liquid oxygen bath the temperature of which was measured by a copper-constantan couple.

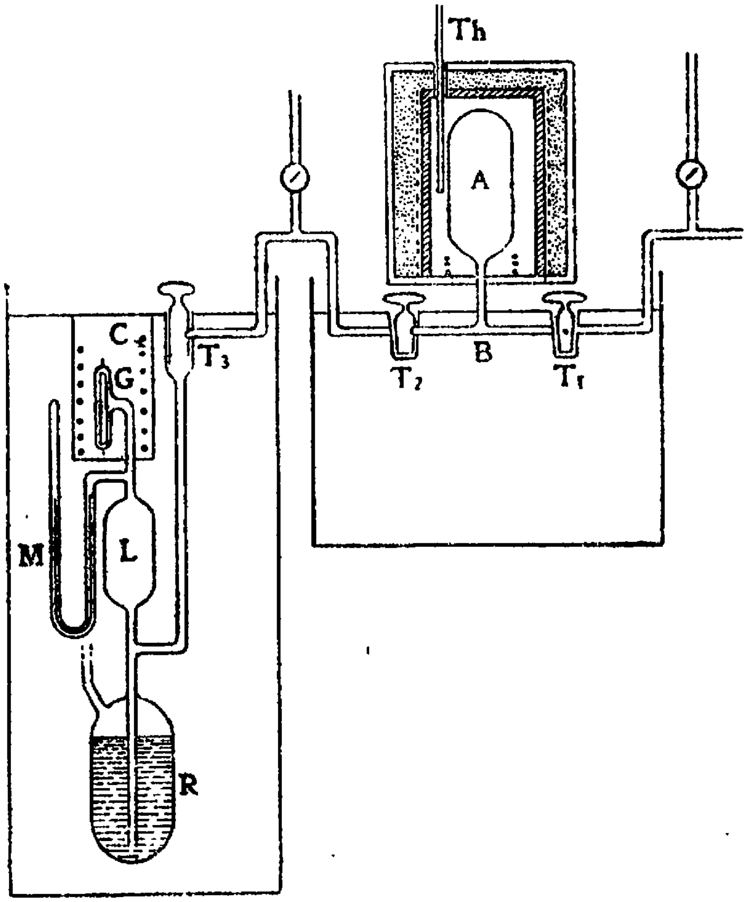

Fig. 1.—Thermal diffusion apparatus (Reproduced from a paper by K. E. Grew, *Proc.* R. *S. L.*, *A*. Vol. 178, p. 391, 1941.)

The gas-mixture at the atmospheric pressure was introduced into the evacuated diffusion vessel through the stopcock T_1. A small part of it was then led into the analyser, previously evacuated, through the stopcock T_2 and its composition determined by a thermal conductivity method to be described in the next paragraph. Sufficient time was then allowed for diffusion to take place. When a steady state was reached the mixture in B was again analysed and the change in the composition determined.

The analyser consisted essentially of a spiral tungsten filament, 2·5 cm. long, welded to short platinum wires which were sealed in 2 mm. capillary tubing as shown at G. A capillary side-tube led to a bulb L of capacity 15 c.c. and a mercury reservoir R. By raising or lowering the level of mercury in the reservoir the pressure of the gas could be adjusted to any desired value indicated by the mercury manometer M. The whole thing was immersed in a paraffin thermostat maintained at 21·2°C by a toluene regulator.

The analysis rests on the fact that the temperature of the filament depends both on the current flowing through it and the conductivity of the gas surrounding it. The filament formed one arm of a Wheatstone's bridge, and its temperature coefficient of resistance was first determined by varying the thermostat temperature and using very low currents so as not to produce appreciable heating effects. The second arm of the bridge consisted of thick nickel and manganin wires wound in the form of a coil C surrounding the gauge G. By combining suitable lengths of nickel and manganin wires the second resistance was given the same temperature coefficient as the first so that any random fluctuation of temperature might affect them equally. The resistance of the second arm was made equal to that of the filament when the temperature of the latter was 41·2°C that is, 20°C above the thermostat temperature, and for equal resistances of the remaining two arms a balance point was obtained. On next introducing the gas mixture into the gauge the balance point was disturbed owing to a fall in the temperature of the filament, the amount of fall depending on the composition of the mixture. The potential difference across the bridge was then increased until the temperature of the filament was brought back to 41·2°C and the bridge was balanced. The change in the composition of the mixture could thus be determined from the change in the potential difference required to balance the bridge.

Value of k_T :—A typical set of experimental results is taken from a paper of Atkins, Bastick and Ibbs, on Thermal Diffusion in Mixtures of inert gases, *P. R. S. L.* (A), Vol. 172, p. 142 and illustrated in Fig. 2 reproduced from there. The ordinate represents the experimentally obtained values of k_T calculated from the observed separation by means of equation (14). The abscissa represents concentration of the lighter constituent in percentages i.e. $100 n_{20}$. If the relation $k_T = a n_{10} n_{20} = \alpha(1-n_{10}) n_{20}$ held good throughout the whole range of n_{20} values, the curve would be a parabola, $k_T = 0$ at $n_{20} = 0$ and at $n_{20} = 1$, rising to a maximum at $n_{20} = 50\%$. Curve III shows that this law is not obeyed. For curve III

(He– Kr) we reproduce in Table 2 the experimental values of k_T and α for different concentrations.

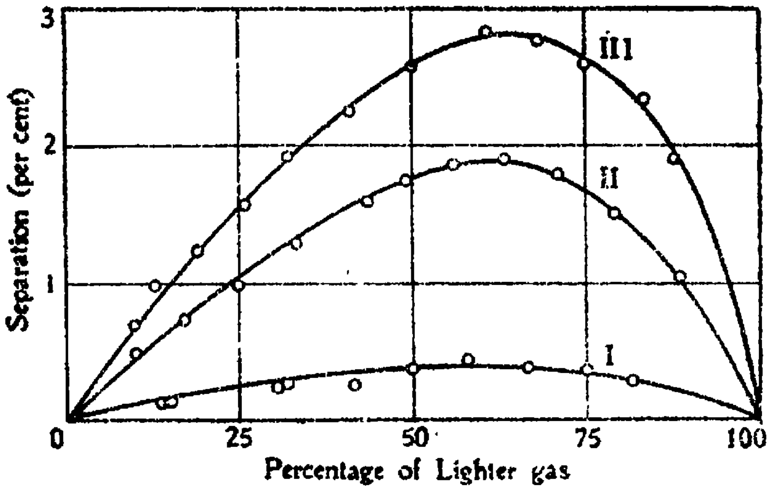

Fig. 2.—Relation between separation and concentration (I, argon-krypton ; II, neon-krypton ; III, helium-krypton)

[Reproduced from a paper by Atkins, Bastick and Ibbs., *P.R.S.L.*, **172**, 148, 1939.]

Table 2.—Thermal diffusion in Helium-Krypton mixture

n_{20}	·3	·4	·5	·6	·7
k_T (experimental)	·0677	·0852	·1000	·1080	·1068
$\alpha = k_T/n_{10}n_{20}$	·323	·355	·400	·450	·509
k_T (rigid sphere)	·105	·133	·156	·172	·176
$\alpha(\infty)$ (from 17)	·500	·559	·624	·716	·838

From Chapman's formulæ, the following first approximation expression has been deduced for α :

$$\alpha = 5(C-1)\,\frac{S_1 n_{10} - S_2 n_{20}}{Q_1 n_{10}^2 + Q_2 n_{20}^2 + Q_{12} n_{10} n_{20}} \quad . \quad . \quad (17)$$

where S_1, S_2, Q_1, Q_2, Q_{12} are functions of m_1, m_2, and the parameters of molecular interaction—the force index s or the molecular diameter etc.; C depends only upon the interaction between unlike molecules. Methods for their calculation have been given by Chapman.

For the case of rigid elastic spheres $5(C-1)=1$, and S_1, S_2, Q_1, Q_2, Q_{12} are found to depend only upon the molecular masses and diameters. The calculated values of k_T and α for the helium-krypton mixture are given in Table 2, rows 3 and 4, assuming that the molecules behave as rigid elastic spheres. Comparison between rows 2 and 4 shows clearly that the rigid sphere model is inadequate for explaining thermal diffusion. In fact both the rigid sphere model and the inverse power model fail badly in case of thermal diffusion in that they give α to be independent of temperature, while experiments show that α is strongly dependent on temperature.

This temperature dependence of α has been investigated extensively by Grew[1] for a number of mixtures and the results explained satisfactorily on the Lennard-Jones (12, 6) model (p. 172), by assuming suitable values of the potential parameters ϵ_{12} and σ_{12} for unlike molecules. In fact, taking advantage of the result that the temperature dependence of α is almost wholly governed by the term $(C-1)$, Srivastava and Madan[2] have developed a method of evaluating the unlike potential parameter ϵ_{12} from the observed temperature variation of α. To a fair approximation the unlike parameters can be calculated from the empirical relations $\epsilon_{12} = (\epsilon_{11} \cdot \epsilon_{22})^{1/2}$ and $\sigma_{12} = \frac{1}{2} (\sigma_{11} + \sigma_{22})$.

When we take isotopes having nearly equal atomic weights, the value of α is extremely small, e.g. for the separation of N_2^{14} and $N^{14}N^{15}$, $\alpha(\infty) = \cdot 89 \times \frac{1}{57} = \cdot 015$; taking the force factor, α actually reduces to $\cdot 0089$ and q the separation factor is equal to $(T_2/T_1)^{\alpha} = 1 \cdot 006$ for a temperature ratio of two i.e. in a stationary apparatus like this, very little separation is effected. In fact, it is much less efficient than other methods (gaseous diffusion p. 206, or chemical exchange reaction). But Clusius and Dickel[3] devised an experimental method which completely revolutionised the technique of separation by the use of this method. It is described in the next section.

4. The Separating Column of Clusius and Dickel.—The apparatus consists of a long cylindrical vertical tube (Fig. 3) about 1 cm. in diameter along the axis of which is stretched a platinum wire which is kept taut by means of the weight of a heavier rod dipping in mercury below. This is kept heated to about 900°C. The tube is enclosed in a concentric jacket through which cold water or some other coolant is circulated. The gaseous mixture is introduced through two side-tubes, which are then closed. It is found that soon after, there is a separation, the light gas quickly collects at the top, and the heavy gas at the bottom. For example, if we have a mixture of H_2 and Br_2 the bromine will collect at the bottom, as is proved by the intense coloration characteristic of Br_2, while H_2 collects at the top. This is shown by the fact that the upper half of the Pt-wire which was glowing loses its glow, showing a rapid fall of temperature, for hydrogen being a much better conductor of heat than the heavy H_2—Br_2 mixture, carries all the heat away and does not allow the wire to attain a high enough temperature for glowing, though the same amount of energy is being applied.

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[1] *Proc. Roy. Soc. Lond.*, **189**, 402, 1947 ; Grew, Johnson and Neal *Proc. Roy. Soc.* **224**, 513, 1954.

[2] *Proc. Phys. Soc. London*, A, **66**, 277, 1953.

[3] *Naturwiss*, **26**, 546, 1938; **27**, 148, 1939.

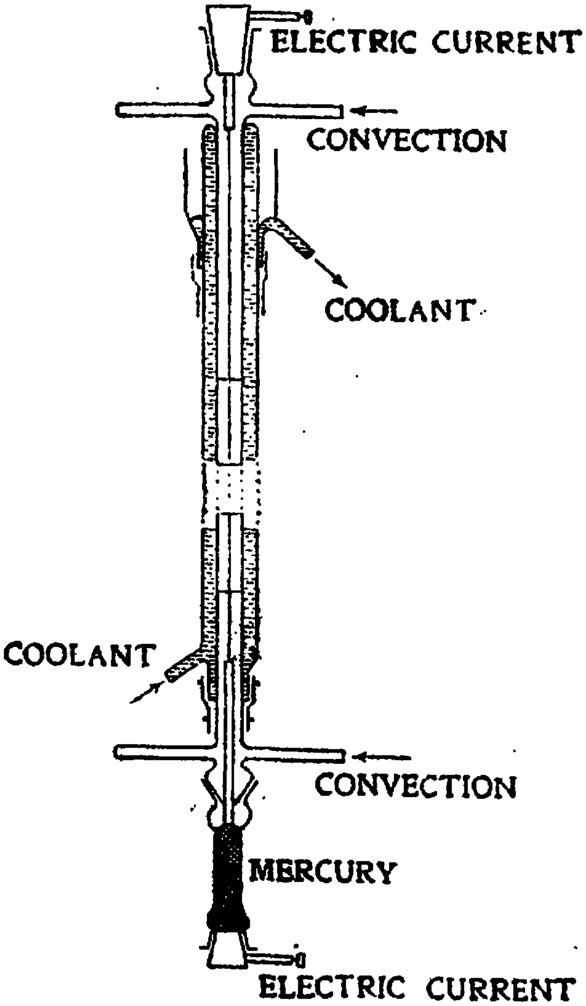

Fig.3.—Separating Column of Clusius and Dickel

The theory of the column is mathematically very complicated and consequently Clark Jones and Furry[1] have given an elementary theory which brings out very clearly the physical processes in the column and which will therefore be discussed here. The working of the column is briefly as follows:—As the gas comes in contact with the hot wire, it gets heated, and a convective circulation of the gas, consisting of the vertical up-streaming of the hot gas near the wire, and down-streaming of the cold gas near the jacket sets in. Therefore the problem is considered in two parts: (1) the purely hydrodynamical problem of convective flow in the column, and (2) the determination of the net transport along the column.

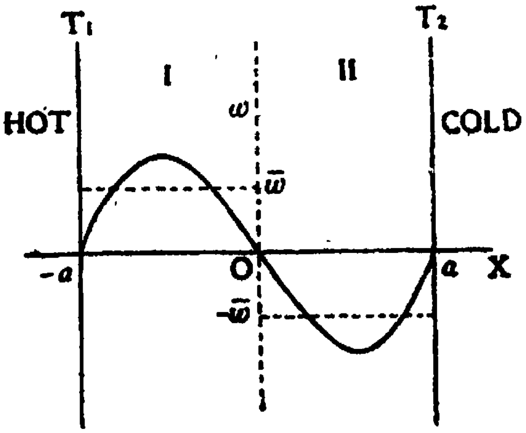

Fig. 4.—Convection currents between the hot and cold walls in the separating column.

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[1] *Rev. Mod. Phys.*, **18**, 151, 1946.

The value of the convection velocity can be easily obtained in the two-dimensional case. Let the cross-section in the xy plane of the vertical column (axis of z) be rectangular with sides of lengths $2a$ and b and let us take the centre of the rectangle as the origin of co-ordinates (Fig. 4). Let the walls $x=-a$, and $x=a$ be maintained at the temperatures T_1, T_2, $(T_1>T_2)$ so that

$$-dT/dx=(T_1-T_2)/2a=\triangle T/2a.$$

The convective velocity w is parallel to the axis of z but it varies with x. The value at any point x can be obtained from the hydrodynamical equations:

$$\frac{dp}{dx}=0,\ \frac{dp}{dz}=-\rho g+\eta\frac{d^2w}{dx^2},$$

where ρ and η are respectively the density and viscosity of the mixture. This last term is due to the transference of momentum of the gas due to viscosity. Now from the condition $\frac{d^2p}{dzdx}=\frac{d^2p}{dxdz}$, we have

$$\eta\frac{d^3w}{dx^3}=g\frac{d\rho}{dx}.$$

Now $\rho\propto 1/T$, hence

$$\frac{d\rho}{dT}=-\frac{\rho}{T},\quad \frac{d\rho}{dx}=\frac{d\rho}{dT}\cdot\frac{dT}{dx},$$

and hence

$$\frac{d^3w}{dx^3}=-\frac{g\rho}{2\eta a}\frac{\triangle T}{T}.$$

T is a function of x but to simplify matters we may assume it to be constant and equal to the mean value $\bar{T}=(T_1+T_2)/2$. The boundary conditions are that $w=0$ at $x=\pm a$. This gives us on integration

$$w=-\frac{g\rho}{12\eta a}\frac{\triangle T}{T}\{x(a^2-x^2)\}\quad .\quad .\quad .\quad .\quad (18)$$

w varies with x and has an extremum value at $x=\pm a/\sqrt{3}$. The mean speed over the range $x=0$ to $x=a$ is

$$\bar{w}=\frac{\rho g}{48\eta}\frac{\triangle T}{T}a^2.\quad .\quad .\quad .\quad .\quad .\quad (19)$$

We shall assume that the gas in the region II from O to the cold plate moves down with this velocity $\bar{w}$ and in region I moves up with the same velocity.

If the number density n_1 in the downward stream is n_1' and in the upward stream n_1'', the net transport down the column is

$$(n_1' - n_1'')\,\bar{w}\,ab + n\,D_{12}\,\frac{dn_{10}}{dz}\,2ab,$$

since the longitudinal diffusion takes place across the whole length $2a$. The mass of molecules (1) transported downwards is

$$\tau_1 = \rho(n_{10}' - n_{10}'')\,\bar{w}\,ab + \rho D_{12}\,\frac{dn_{10}}{dz}\,2ab. \qquad . \quad . \quad (20)$$

The concentrations n_{10}', n_{10}'' are actually produced by the combined effect of vertical convection and transverse diffusion (thermal and ordinary). Due to the former n_1' decreases by $-\bar{w}\,dn_1/dz$ per second, n_1'' increases by $-\bar{w}\,dn_1/dz$; hence $(n_1' - n_1'')$ decreases by $-2\bar{w}\,dn_1/dz$. Due to the latter the number flux density of molecules (1) is given by (11), and as this flux is into a layer of thickness a, n_1' increases at the rate Γ_1/a, and n_1'' decreases at the same rate, and therefore $n_1' - n_1''$ increase at the rate $2\Gamma_1/a$. In the steady state the net increase from both causes must vanish, i.e.

$$\frac{2\Gamma_1}{a} + 2\bar{w}\,\frac{dn_1}{dz} = 0. \qquad . \quad . \quad . \quad (21)$$

Substituting Γ_1 from (11) and writing

$$\frac{dn_{10}}{dx} = \frac{n_{10}' - n_{10}''}{a}, \quad \frac{dT}{dx} = -\frac{\Delta T}{2a},$$

equation (21) yields

$$n_{10}' - n_{10}'' = \alpha n_{10} n_{20}\,\frac{\Delta T}{2\bar{T}} + \frac{\bar{w}a^2}{D_{12}}\,\frac{dn_{10}}{dz}, \qquad . \quad . \quad . \quad (22)$$

and substituting this in (20) we get

$$\tau_1 = \rho\bar{w}\,ab\left[\alpha n_{10} n_{20}\,\frac{\Delta T}{2\bar{T}} + \frac{aw}{D_{12}}\,\frac{dn_{10}}{dz}\right] + \rho D_{12}\,\frac{dn_{10}}{dz}\,2ab$$

$$= H n_{10}\,n_{20} + (K_c + K_d)\,dn_{10}/dz, \qquad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where $$H = \frac{\alpha\rho^2 g a^3 b}{96\eta}\left(\frac{\Delta T}{T}\right)^2, \quad K_c = \frac{\rho^3 g^2 a^7 b}{48^2\eta^2 D_{12}}\left(\frac{\Delta T}{T}\right)^2$$

$$K_d = \rho D_{12}.\ 2ab.$$

The three terms respectively represent the contribution of thermal diffusion, convection and longitudinal diffusion.

After sufficient time a steady state is reached when the transport $\tau_1 = 0$. Then

$$H n_{10}\,n_{20} = -\,K\,\frac{dn_{10}}{dz}\,, \qquad . \quad . \quad . \quad . \quad . \quad (24)$$

where $K = K_c + K_d$. Integrating we get

$$\left(\frac{n_{10}}{n_{20}}\right)_z = \left(\frac{n_{10}}{n_{20}}\right)_0 e^{-2zA}, \quad . \quad . \quad . \quad . \quad (25)$$

where $A = H/2K$. The separation factor is

$$q_e = e^{2AL} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

for a column of length L. The rigorous theory which takes into account the variation of n, η, D_{12} etc with temperature and variation of w with x produces only a change in the numerical factor occurring in the expression for A.

For the production of a large separation the column must be long and A should be large, i.e. the ratio of the thermal diffusion as represented by H to the remixing effect as represented by K should be large. In practice due to small irregularities in dimensions and temperature distribution in the column some additional remixing effect occurs which is represented by the term K_p, and therefore $K = K_c + K_d + K_p$. When this value of K is substituted, equation (26) is found to hold fairly well.

The performance of a typical Clusius column is illustrated by Fig. 5, which represents the working of a typical 20 metre column of the type illustrated in Fig. 3. This was used for the separation of the isotopes of chlorine; they have the atomic weights 34·979 and 36·956 and occur in the proportion of 75 : 25. Actually HCl gas was used. After steady conditions had set in, probes of the gas were taken at different points and its isotopic composition was analysed by density determinations. Fig. 5 shows the distribution of the lighter constituent at different heights of the column. It shows clearly as equation (25) indicates that the proportion of Cl^{35} goes on increasing with height, and at 20 metres, we have nearly 99·6% of pure Cl^{35}. It was found that to separate one mole of chlorine completely the amount of energy needed was nearly 43000 K.W.H.

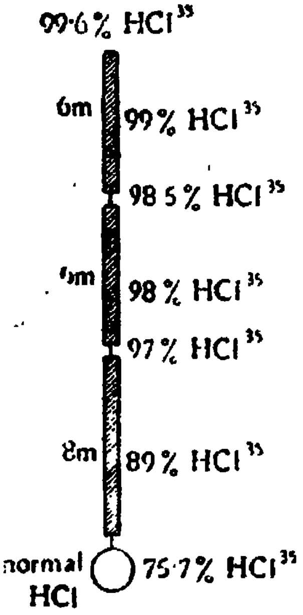

Fig. 5.—Performance of a Clusius column.

The task of separation of isotopes has now assumed industrial proportions, not only for the production of the raw material for atomic energy fuel (this is used in the form of UF_6 which is gaseous) but also on account of the need for particular isotopes for researches in nuclear physics, in biology, and other branches of science. C^{13}, N^{15} and several others are being produced on the commercial scale and offered for sale.

In many cases, other methods have been found more suitable, (e.g. gaseous diffusion) but on account of secrecy regulations, it is difficult to find out the actual situation, and make a comparative assessment of the merits of different methods.

Literature :—For further information, see *Ergebnisse der exakten Naturwissenschaften*, Vol. 20, article on *Trennrohr*, by Fleischmann and Jensen, p. 121-182, or a report in the *Reviews of Modern Physics*, Vol. 18, on the "Separation of Isotopes by Thermal Diffusion" by Jones and Furry.

NOTE 19

Occurrence of Elements and their Isotopes on the Earth, the Meteorites, the Sun and the Stars.

This is a purely 'cosmological problem', but has cropped up here only as a side issue. Only the briefest outline will be given.

The Earth—Extensive chemical and spectroscopic investigations have been undertaken on the composition of the rocks forming the outer crust of the Earth, on the composition of its atmosphere, and the composition of matter in solution in sea water. These results have been summarised by Goldschmidt and others, and are given in Table 1 below. It should be borne in mind that different kinds of rocks have different composition. The figures given here are average ones and for understanding how these have been obtained, the reader must refer to original papers. No figures are given for H, He, C and N and a few others. All free hydrogen must have escaped from the primitive atmosphere of the earth, as the kinetic energy of the molecules at the high temperature prevailing in those times was too high for their detention (see p. 136). The hydrogen now found on earth occurs almost completely as a component of water, which must have been deposited from water vapour, or released from rocks as they cooled. If the primitive earth contained any helium, it must have been completely lost, and the little helium we get now is probably wholly obtained from radioactive disintegration. Carbon is largely found in organic matter, either living or fossilized (coal and petrol) and nitrogen almost wholly in organic matter and in the atmosphere.

The abundance for other elements is given in terms of number of atoms taking that of Fe as 100. The most abundant elements are

Table 1. — *Abundance of Elements in the earth's crust, meteorites and the Sun*[1].
Fe=100

		Earth's crust	Iron Meteors	Sun			Earth's crust	Iron Meteors	Sun
1	H			6×10^{5}U	41	Nb	·017	·0^{4}5	·0^{4}6 R
2	He				42	Mo	·017	·001	·0^{2}12 U
3	Li	1·0	·0035	·0^{3}6 R	44	Ru		·0^{3}51	·0^{3}2 R
4	Be	·07	·0^{3}813	·0^{3}4	45	Rh	·0^{2}1	·0^{3}19	·0^{4}2 R
5	B	·03	·0^{2}22	·63 R	46	Pd	·0^{4}1	·0^{3}17	·0^{4}8 R
6	C		·72	3700	47	Ag	·0^{3}1	·0^{5}15	·0^{4}6 R
7	N		·0^{3}8	776 U	48	Cd	·0^{3}48	·0^{4}14	·001 R
8	O	3400	185	1023 U	49	In	·0^{3}1	·0^{4}5	·0^{5}6 R
9	F	1·5	·018	6 R	50	Sn	·037	·0^{2}34	·0^{3}1 R
10	Ne				51	Sb	·0^{3}9	·0^{3}1	·0^{4}4 R
11	Na	135	2·5	3·63 U	53	I	·0^{3}26	·0^{3}1	
					55	Cs	·0^{2}58	·0^{5}5	
12	Mg	94	·48	62 U	56	Ba	·311	·0^{3}2	·0^{2}17 U
13	Al	358	4·8	4·1 U	57	La	·015	·0^{3}1	·0^{3}4
14	Si	1076	54·64	37·16 U	58	Ce	·032	·0^{3}12	·0^{2}16 R
15	P	2·8	·7	·063 R	59	Pr	·00435	·0^{4}5	·0^{4}25 R
16	S	1·7	4·12	45·8 U	60	Nd	·0183	·0^{3}18	·0^{3}6 R
17	Cl	1·5	·17		62	Sm	·0^{2}47	·0^{4}65	·0^{3}2 R
18	Ar				63	Eu	·0^{3}74	·0^{3}15	·0^{3}16 R
19	K	72	·38	·30 U	64	Gd	·0^{2}438	·0^{3}1	·0^{4}8 R
20	Ca	99	3·66	3·23 U	65	Tb	·0^{3}69	·0^{4}28	
21	Sc	·12	0·09	·004 U	66	Dy	·0^{2}29	·0^{3}11	·0^{3}25 R
22	Ti	14·4	·14	·17 U	67	Ho	·0^{3}8	·0^{4}31	
23	V	·21	·013	·021 U	68	Er	·0^{2}16	·0^{4}88	·0^{3}8 R
24	Cr	·42	·52	·72 U	69	Tu	·0^{3}2	·0^{4}16	·0^{4}2 R
25	Mn	1·85	·42	5·5 U	70	Yb	·0^{2}16	·0^{4}82	·0^{4}63 R
26	Fe	100	100	100·00U	71	Lu	·0^{3}44	·0^{4}26	·0^{4}63 R
				100·00R	72	Hf	·019	·0^{4}38	·0^{5}16 R
27	Co	·074	·026	·2 U	73	Ta		·0^{4}17	·0^{6}63 R
28	Ni	·186	7·3	1·7 U	74	W	·041	·0^{3}93	·0^{5}1 R
29	Cu	·172	·025	·032U	75	Re	·0^{7}7	·0^{4}22	
30	Zn	·067	·0087	·11 U	76	Os		·0^{3}19	·0^{5}2 R
31	Ga	·023	·0^{3}35		77	Ir	·0^{7}6	·0^{4}76	·0^{6}4 R
32	Ge	·015	·0136	·0063R	78	Pt	·0^{6}3	·0^{3}47	·0^{4}25 R
33	As	·0^{2}7	·026		79	Au	·0^{6}3	·0^{4}45	
34	Se	·0^{2}1	·0^{2}13		80	Hg	·0^{3}27		
35	Br		·0023		81	Tl	·0^{3}24		
37	Rb	·397	·0^{3}4	·0^{3}3 R	82	Pb	·0085	·0^{4}15	·0^{3}67 U
38	Sr	·52	·0022	·0042 U	83	Bi	·0^{3}1	·0^{4}12	
39	Y	·038	·0^{3}54	·0031 U	90	Th	·0052	·0^{4}6	
40	Zr	·23	·0082	·0^{3}45 U	92	U	·0018	·0^{4}14	

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[1] R stands for Russell, U stands for Unsöld.

O, Si, Mg, Fe, Al, Ca, Na, K. The other elements will hardly afford ·2 atoms, all told.

Meteorites: They are the 'Fire balls' which flash across the sky, and are found in weights ranging from a few milligrams to a few tons. They are found to be of two types: Iron meteorites, and Stony meteorites. The analysis of iron meteorites shows that they are on the average 90% iron, 8% nickel, and 2% others. The high proportion of nickel to iron is a mystery yet. There is very little siliceous matter.

The stony meteorites consist mainly of magnesium and iron silicates. Most stony meteorites have finely divided metals distributed throughout the mass. On an average the metal phase constitutes about eleven percent, but the quantity of metals in some cases varies from zero to about fifty percent. A third and less abundant phase (troilite) mainly composed of FeS exists in both iron and stony meteorites, usually distributed over the whole mass but frequently found in pockets of substantial size.

According to one school of thought, the earth's interior is a liquid mass. This is borne out by evidence from seismology, for transversal seismic waves fail to be transmitted when they reach a distance of 3400 km. from the core. This inner core is supposed to consist entirely of liquid iron and nickel, in the proportion of 100 to 7·5 as in iron meteorites and the external crust is supposed to consist mainly of siliceous matter originally dissolved in it. As the core cooled, it separated out in the form of a slag, having approximately the same composition as the stony meteorites. The outer parts of the slag formed the crust.

The Sun—The abundance of elements in the sun is given in terms of the number of atoms found over a cm^2 of its photosphere. This figure is obtained from a complicated analysis of the strength of the Fraunhofer line or lines by which the element is identified, the position of the line in the spectral series of the element, and other points for which a reference must be made to original papers. See Unsöld, *Zeits. f. Astrophysik*, Vol. 24.

Very great precautions have to be taken in deducing any conclusions about the abundance of elements in the sun and other stellar bodies. The absence of the lines of an element must not be taken to imply that the element is actually absent; it may be that the element, as in the case of Rb and Cs is completely ionised, and the lines of the ionised element are not within the available range (λ 3000–10000). Let us now scrutinise the eleme

(1) The halogens, excepting F.—Their resonance lines are in the extreme ultraviolet. The next lines (e. g. for $p^4s—p^4p$) are in the extreme red, but they have not been found. No compounds containing halogens are found in stellar atmospheres.

(2) The rare gases excepting helium.—Resonance lines lie in the extreme ultraviolet; next lines $p^5s—p^5p$ are in red and infra-red, but they have not been found in any stellar spectrum.

(3) Generally heavy elements.—The heaviest element known on the sun is Pb. Bismuth which is 80 times less abundant on the earth is not found, though its resonance lines are in a very good region. The fissionable element Th has recently been identified by Babcock by means of its ionised lines. Uranium may also occur but its spectrum is not yet so well known.

It is believed that if the sun were cooled to the temperature of the Earth, the composition of its crust would not be much different from that of the Earth.

The Balmer lines of hydrogen are found in great strength in the atmosphere of the sun and all stars. From this and other reasons it has been concluded that it is the most abundant element in all heavenly bodies and also in interstellar space, but estimates as to its abundance vary widely. For the sun's atmosphere, Unsöld gave the proportion as

	H	O	Metals	Electrons
Proportion in no. of atoms	91	3·3	3·3	2·4

The absolute amount is given as 3×10^{24} atoms, giving a total mass of 5 gm. over 1 cm^2 of the photosphere. Taking the number of Fe-atoms as 100, the number of H-atoms comes to be nearly 10^6. But recent investigations by Wildt and Chandrasekhar have raised the proportion of H to the rest (excepting He, O and N) as 4000 : 1. It appears that He, N, O and probably one or two more have to be left out of general considerations.

In the calculation of the ionisation of the elements in the sun the value of electron pressure plays a great part. This pressure has been estimated to be about 10 dynes on the reversing layer, giving an electron density of 10^{13} per c.c. on the disc. The electrons are almost wholly derived from the ionisation of the metals. H, He, O and N are not ionised appreciably on account of their high ionisation potential.

NOTE 20

Table 1.—*Properties of Ammonia* (NH$_3$)

Temp. °C	Vapour Pressure in lb. per sq. in. p	Volume of saturated vapour in cu. ft. per lb.	Enthalpy of liquid in lb-calories (*C.H.U.*) per lb. h	Latent Heat of saturated vapour in *C. H. U.* per lb. L	Enthalpy of vapour in *C. H. U.* per lb. h	Entropy	
						Liquid	Vapour
—10	41·5	6·8	—8	322	314	–0·033	1·193
—5	51	5·6	—4·5	319·5	315	–0·017	1·175
0	61	4·7	0	316	316	0·0	1·158
5	74·5	4·7	4·5	312·5	317	0·017	1·141
10	89	3·3	9·2	308·6	317·8	0·033	1·123
15	106	2·7	14	304	318·8	0·050	1·107
20	125	2·3	18·6	300	318·6	0·066	1·089
30	170	1·7	28·2	290	318·2	0·098	1·055

Table 2.—Properties of Dry Saturated Steam.

Temp. °C	Pressure in lb. per sq. in. *p*	Volume in cu. ft. per lb.		Enthalpy of water in lb-calories per lb. *h*	Latent Heat of steam in lb-calories per lb. *L*	Total Heat of steam in lb-calories per lb.	Internal energy in lb-calories per lb.	Entropy per lb.	
		Dry steam	Water					Water	Steam
0	0·0892	3275·9	0·01602	0·0	594·27	594·27	564·21	0·0	2·17602
10	0·1788	1693·9	0·01603	9·98	589·03	599·01	567·85	0·03585	2·11650
20	0·3400	922·2	0·01605	19·94	583·78	603·72	571·48	0·07046	2·06220
30	0·6162	525·8	0·01609	29·91	578·49	608·40	575·07	0·10393	2·01248
40	1·0703	312·4	0·01614	39·89	573·15	613·04	578·64	0·13631	1·96688
50	1·7883	292·7	0·01621	49·88	567·75	617·63	582·17	0·16770	1·92490
60	2·8873	122·9	0·01629	59·87	562·29	622·16	583·66	0·19815	1·88620
70	4·5156	80·8	0·01638	69·88	556·72	626·60	589·07	0·22774	1·85039
80	6·8627	54·6	0·01648	79·90	551·05	630·95	592·41	0·25652	1·81713
90	10·161	37·82	0·01659	89·94	545·25	635·19	595·67	0·28454	1·78619
100	14·689	26·79	0·01671	100·00	539·30	639·30	598·83	0·31186	1·75732
120	28·808	14·271	0·01698	120·22	526·85	647·07	604·78	0·36460	1·70485
140	52·482	8·143	0·01729	140·62	513·57	654·19	610·23	0·41511	1·65832
160	89·80	4·923	0·01765	161·26	499·29	660·55	615·08	0·46373	1·61657
180	145·59	3·128	0·01807	182·21	483·93	666·14	619·30	0·51078	1·57884
200	225·24	2·074	0·01856	203·55	467·41	670·96	622·91	0·55654	1·54452
220	334·38	1·428	0·01914	247·74	449·69	675·06	625·93	0·60128	1·51326
240	478·74	1·018	0·01980	225·37	430·81	678·55	628·43	0·64517	1·48479

Table 3.—Entropy and Enthalpy of Superheated Steam.

Pressure Absolute lb. per sq. in.	Entropy at Superheat in degrees C					Enthalpy at Superheat in degrees C				
	+20	+40	+60	+80	+100	+20	+40	+60	+80	+100
15	1·7817	1·8062	1·8295	1·8515	1·8725	649·53	659·43	669·25	679·04	688·78
20	1·7590	1·7832	1·8061	1·8279	1·8486	652·91	662·90	672·79	682·63	692·42
40	1·7045	1·7282	1·7505	1·7716	1·7918	661·37	671·61	681·73	691·76	701·69
60	1·6728	1·6961	1·7182	1·7390	1·7589	666·44	676·89	687·20	697·37	707·45
80	1·6503	1·6736	1·6954	1·7161	1·7358	670·07	680·73	691·18	701·49	711·68
100	1·6329	1·6560	1·6778	1·6984	1·7179	672·88	683·70	694·30	704·73	715·03
120	1·6187	1·6418	1·6635	1·6840	1·7034	675·19	686·14	696·88	707·42	717·81
140	1·6066	1·6297	1·6513	1·6717	1·6911	677·13	688·23	699·08	709·73	720·20
160	1·5962	1·6194	1·6409	1·6618	1·6806	678·77	690·01	700·98	711·72	722·28
180	1·5870	1·6101	1·6317	1·6520	1·6713	680·24	691·60	702·66	713·51	724·16
200	1·5787	1·6018	1·6234	1·6437	1·6630	681·52	693·00	704·17	715·15	725·82
250	1·5612	1·5843	1·6059	1·6262	1·6454	684·23	695·97	707·38	718·10	729·41
300	1·5468	1·5700	1·5967	1·6120	1·6312	686·40	698·39	710·01	721·32	732·38
350	1·5348	1·5580	1·5797	1·6000	1·6191	688·22	700·44	712·24	723·72	734·93
400	1·5243	1·5476	1·5693	1·5896	1·6087	689·77	702·19	714·16	725·81	737·17
450	1·5150	1·5384	1·5601	1·5805	1·5996	691·12	703·72	715·88	727·65	339·14
500	1·5068	1·5302	1·5519	1·5723	1·5915	692·32	705·09	717·40	729·32	740·93

NOTE 21

The Thermodynamics of Irreversible Processes

In Chapters V to VIII we have described the thermodynamics of reversible processes which was based on the three laws of thermodynamics. These were first taken to be basic principles but were later on derived by statistical methods from the laws of mechanics (Chap. IX), and thus thermodynamics as applied to equilibrium systems and reversible changes became a branch of statistical mechanics. There are, however, various non-equilibrium phenomena characterised by irreversible processes which cannot be explained, except qualitatively, by these three laws. The purpose of this note is to formulate a macroscopic theory for such non-equilibrium processes. It has been found that if the system is close to equilibrium, it is possible to describe in general terms its rate of approach to equilibrium by means of certain principles. These principles and their formulation are known as the thermodynamics of irreversible processes, which has been successfully applied to various irreversible phenomena though it must be admitted, it has not yet attained the firm foundation of the equilibrium theory.

Consider some equation which describes a time-dependent physical process. If the equation is invariant with regard to the algebraic sign affixed to the variable time, the process is called a reversible process, otherwise it is called irreversible. Most of the physico-chemical processes are irreversible, and the major progress in thermodynamics during the last twenty years is related to the extension of macroscopic method to such processes. It will be noticed that the usual phenomenological laws describing irreversible processes exist in the form of proportionalities, e.g. Fourier's law between heat flow and temperature gradient (Chapters III and XIV), Fick's law between flow of matter of one component and its concentration gradient (Chap. III), Newton's law between shearing force and velocity gradient, Ohm's law between electric current and potential gradient etc. When two or more of these phenomena occur simultaneously, they interfere and give rise to new effects. Thus the coupling of diffusion and heat conduction gives rise to thermal diffusion (Soret effect) and its inverse the Dufour effect. The cross-phenomena are mathematically described by additional linear terms. We shall now give an outline of Onsager's theory upon which the thermodynamics of irreversible processes is based.

The Linear Law: The thermodynamics of irreversible processes is based upon two important concepts: (1) the linear law and (2) the Onsager reciprocal relations. The linear law is a generalisation of the empirical relations which are found to hold for many systems only slightly removed from equilibrium. At the present time the linear law is only empirical and has no foundation except as a working postulate which is justified by the results. However it is possible to study the approach of a system to equilibrium with the help of the statistical theory of fluctuations and it is very likely that the linear law can be justified on this basis. Linear relations should almost always apply sufficiently close to equilibrium; in effect, therefore this postulate of linear relationship merely defines the range of applicability of the thermodynamics of irreversible processes.

We have seen above that a number of causes can give rise to occurrence of irreversible phenomena, e.g. a temperature gradient produces heat flow, a concentration gradient produces diffusion flow etc. These causes are called driving "forces" or "affinities" (usually denoted by X) which produce "fluxes" (also called "flows" or "rates" and usually denoted by J) and thereby tend to restore the system to equilibrium. In general any force can give rise to any flow e.g. a temperature gradient can produce heat flow as well as diffusion flow. Hence for situations not too far removed from equilibrium the irreversible phenomena can be expressed by linear relations of the general type

$$J_i = \sum_{k=1}^{n} L_{ik} X_k \quad (i = 1, 2, \ldots, n). \quad . \quad . \quad . \quad (1)$$

which states that the fluxes are linear functions of the generalised forces. Linear relations of this type are called phenomenological relations and the coefficients L_{ik} are called the phenomenological coefficients. The coefficients L_{ii} may stand for the heat conductivity, the ordinary diffusion coefficient, the electrical conductivity etc., while the coefficients L_{ik} $(i \neq k)$ describe the interference of the two irreversible processes i and k. If for example the two processes are thermal conductity and diffusion, the coefficient L_{ik} is connected with thermodiffusion. It is in the study of these interference effects that the thermodynamics of irreversible processes has been very useful. Considering only two simultaneous irreversible processes, equation (1) may be written down

$$\left.\begin{aligned} J_1 &= L_{11} X_1 + L_{12} X_2 \\ J_2 &= L_{21} X_1 + L_{22} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (2)$$

Onsager reciprocal relations: We shall now formulate the fundamental theorem of the thermodynamics of irreversible processes due to Onsager. This theorem states that *if a "proper choice" of the fluxes J_i and forces X_i has been made, the matrix of phenomenological coefficients L_{ik} is symmetric i.e.*

$$L_{ik} = L_{ki} \quad (i, k = 1, 2, \ldots n) \quad . \quad . \quad . \quad . \quad (3)$$

These identities are called the Onsager reciprocal relations, which in the thermodynamics of irreversible processes play a role similar in importance and in concept to the second law. We must however explain what is meant by a "proper choice" of the fluxes and forces. Let us suppose that the state of the system is described by a number of parameters A_1, A_2, ... A_n (these may be the *local* temperature, pressure etc.), and the values of these parameters in the state of thermodynamic equilibrium are A_1°, A_2°..... A_n°. For convenience we use the deviations of the state parameters from their equilibrium values viz. $a = A_i - A_i^\circ$ with $i = 1, 2, \ldots . n$, as our state variable. It will be shown later that the "proper choice" of the fluxes and forces are respectively the time derivative of the state variables a_i:

$$J_i = \dot{a}_i \quad (i = 1, 2, \ldots . , n) \quad . \quad . \quad . \quad (4)$$

and the following linear combinations of the state variables a_i:

$$X_i = \frac{\partial(\triangle S)}{\partial a_i} \quad (i = 1, \; 2, \ldots . n). \quad . \quad . \quad . \quad . \quad (5)$$

where $\triangle S$ denotes the deviation of the entropy from its equilibrium value.

Due to the irreversible processes there will be entropy production in the system. The change in entropy $\triangle S$ from the equilibrium value can always be written down as a function of the parameters a_1, a_2, . . . Hence

$$\dot{\triangle S} = \frac{\partial(\triangle S)}{\partial a_1} \dot{a}_1 + \frac{\partial(\triangle S)}{\partial a_2} \dot{a}_2 + \ldots . .$$

$$= \sum_i \dot{a}_i \frac{\partial(\triangle S)}{\partial a_i} = \sum_i J_i X_i . \quad . \quad . \quad . \quad . \quad (6)$$

from (4) and (5). Fluxes J_i and forces X_i with the same index i are called conjugated parameters. It is possible that the expression $\dot{\triangle S}$ can be split in several ways into a sum of conjugated J_i and X_i but for all the choices made the Onsager relation (3) holds.

Equations (1), (3), (4), and (6) give a complete set of equations upon which a satisfactory macroscopic theory of the thermodynamics of irreversible processes can be built up. We may assume eqn. (3) as a fundamental principle without bothering about its proof and develop the thermodynamics of irreversible processes just as classical thermodynamics is developed from the three basic laws. The inquisitive reader may obtain the statistical proof later if he chooses.

For illustrating the methodology we shall consider a simple system which is composed of two parts both enclosed within the same rigid adiabatic enclosure. One part is at a uniform temperature T_1 and the other at a uniform temperature T_2. Let a small amount of heat δQ flow from the part at T_2 to that at T_1. The increase in entropy of the system is

$$dS = \delta Q\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \delta Q . \frac{T_2 - T_1}{T_1 T_2} .$$

The rate of entropy production is

$$\dot{S} = \frac{\triangle T}{T^2} \dot{Q} \qquad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

if $T_2 - T_1 = \triangle T$, and $T = \sqrt{T_1 T_2}$. Thus the entropy production is a product of two factors : $\dot{Q}$ which represents the flux J_u tending to re-establish equilibrium and $\frac{\triangle T}{T^2}$ which represents the driving force X_u causing the flux and this is in agreement with (6). Eqn. (1) for this case yields

$$\dot{Q} = L \frac{\triangle T}{T^2}, \qquad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

which is the well-known Newton's law of cooling.

Proof of Onsager reciprocal relations : The proof is based on a formal treatment of the kinetics of irreversible processes in general. The statistical mechanical theory of fluctuations together with the concept of microscopic reversibility is utilised and it is assumed that the rate of a macroscopic irreversible process is the same as the average rate of regression of statistical fluctuations in the state of the system. This procedure is outlined below.

We shall first work out the statistical mechanics of fluctuations of an aged system i.e. a system which has been left isolated for a length of time sufficient to ensure thermodynamic equilibrium. Suppose the state of the system is described by a number of characteristic parameters A_1, $A_2, \ldots\ldots, A_n$ (these may be the *local* values of the temperature, pressure, concentration etc.). Because of the continuous variation of the properties in this case the variables form an infinite set. The deviations of these parameters A_i from their equilibrium values A_1° will be denoted by $a_i = A_i - A_i^\circ$ as before. In the equilibrium state the entropy has maximum value and the state variables a_i are zero.

The deviation $\triangle S$ of the entropy from its equilibrium value due to the fluctuation a_i is given by the quadratic expression

$$\triangle S = -\tfrac{1}{2}\sum_{i,\,k=1}^{n} g_{ik}\, a_i\, a_k \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where g_{ik} is a mixed second derivative appearing in a Taylor series and is clearly symmetric. X_i is therefore given by

$$X_i = \frac{\partial(\triangle S)}{\partial a_i} = -\sum_{k=1}^{n} g_{ik}\, a_k \quad . \quad . \quad . \quad . \quad (10)$$

Further $$\dot{\triangle S} = -\sum_{i,k} g_{ik}\, \dot{a}_i\, a_k = \sum_i J_i X_i \quad . \quad . \quad (6a)$$

In the system under consideration the probability P of fluctuations $da_1, da_2, \ldots$ is, from Einstein's fluctuation theory, proportional to the exponential of the corresponding entropy deviation $\triangle S$ divided by Boltzmann's constant k. Hence the probability of finding a state in which the values of a_i lie between a_i, $a_i + da_i$ is given by

$$P da_1 \ldots da_n = \frac{exp\,(\triangle S/k).\, da_1 \ldots da_n}{\int \ldots \int exp\,(\triangle S/k).\, da_1 \ldots da_n} \quad . \quad . \quad (11)$$

The denominator of the right hand ensures normalisation to unity.

$$\int \ldots \int P da_1 \ldots da_n = 1 \quad . \quad . \quad . \quad . \quad (12)$$

We now calculate the following average

$$\overline{a_i X_j} \equiv \int \ldots \int a_i X_j \; P \; da_1 \ldots da_n \quad . \quad . \quad . \quad (13)$$

From (10) and (11) we get

$$\overline{a_i X_j} = k \int \ldots \int \frac{\partial \log P}{\partial a_j}\, P \; da_1 \ldots da_n$$

$$= k \int \ldots \int da_1 \ldots da_{j-1}\, da_{j+1} \ldots da_n \int a_i \frac{\partial P}{\partial a_j}\, da_j \,. \quad . \quad (14)$$

But $$\int_{-\infty}^{+\infty} a_i \frac{\partial P}{\partial a_j}\, da_j = \Big[a_i P\Big]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} P \frac{\partial a_i}{\partial a_j}\, da_j$$

by partial integration. Now P is zero for $a_i = \pm\infty$. Further a_i and a_j are independent variables, hence

$$\frac{\partial a_i}{\partial a_j} = \delta_{ij} \quad \text{with} \quad \delta_{ij} \begin{cases} = 1 \text{ for } i = j \\ = 0 \text{ for } i \neq j. \end{cases}$$

Hence

$$\overline{a_i X_j} = -k \int \dots \int da_1 \dots da_{j-1}\, da_{j+1} \dots da_n \int P \delta_{ij}\, da_j. \qquad (15)$$

Using the normalisation condition (12), eqn. (15) yields

$$\overline{a_i X_j} = k\, \delta_{ij} \quad (i, j = 1, 2, \dots, n). \quad . \quad . \quad . \qquad (16)$$

Now we shall utilise the principle of microscopic reversibility which implies the invariance of all mechanical equations of motion of individual particles with respect to the transformation $t \to -t$. Consider the value of the fluctuation a_i at a time instant t and of fluctuation a_j after a time interval τ and let us form the product of both quantities. The average value of this product during a sufficiently long lapse of time is

$$\overline{a_i(t)\, a_j(t+\tau)} = \lim_{T \to \infty} \frac{1}{T} \int_0^T a_i(t)\, a_j(t+\tau) dt. \quad . \quad . \quad . \qquad (17)$$

From the general principles of statistical mechanics it can be shown that the time average (17) for one single system is equal to the average over a microcanonical ensemble obtained by using the probability function (11) [this is the so-called ergodic hypothesis (p. 393)].

Let us next consider the average value of the product $a_j(t)\, a_i(t+\tau)$. The mean value of this product differs from (17) merely by the substitution $t \to -t$. So we shall express the microscopic reversibility by the relation

$$\overline{a_i(t)\, a_j(t+\tau)} = \overline{a_j(t)\, a_i(t+\tau)}. \quad . \quad . \quad . \qquad (18)$$

Subtracting the same quantity $\overline{a_i(t)\, a_j(t)}$ from both sides and dividing by τ, we get

$$\overline{a_i(t) \frac{[a_j(t+\tau) - a_j(t)]}{\tau}} = \overline{a_j(t) \frac{[a_i(t+\tau) - a_i(t)]}{\tau}}$$

When τ tends to zero, this yields

$$\overline{a_i(t)\, \dot{a}_j(t)} = \overline{a_j(t)\, \dot{a}_i(t)}. \quad . \quad . \quad . \quad . \qquad (19)$$

The time derivative in (19) denoted by the dot, must be considered as a quotient of differences taken over a time τ-large in comparison to the time interval between two collisions of molecules.

Onsager next makes the important assumption, which is a new hypothesis, that on the average the decay or regression of a fluctuation follows the ordinary phenomenological macroscopic laws (1) and hence we can write

$$J_i = \dot{a}_i = \Sigma L_{ik} X_k. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

Substituting (20) in (19) we get

$$\overline{\sum_k L_{jk}\, a_i\, X_k} = \overline{\sum_k L_{ik}\, a_j\, X_k}. \quad . \quad . \quad . \quad . \quad (21)$$

Using (16) this yields

$$k \sum_k \delta_{ik}\, L_{jk} = k \sum_k \delta_{jk}\, L_{ik},$$

or, since $\delta_{ij}=0$ for $i \neq j$,

$$L_{ji} = L_{ij} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

which is the Onsager relation.

Application.—The thermodynamics of irreversible processes has been applied extensively to elucidate a large number of irreversible phenomena, particularly cross-phenomena where it is most useful, and the detailed treatments can be found in a number of books[1] now available. We shall explain the method here by taking a simple example.

Consider an adiabatically insulated system composed of two vessels I and II maintained at two temperatures, T and $T+\triangle T$, and communicating with each other through a hole. For a Knudsen gas this is the well-known phenomenon of thermal transpiration and as shown in §3·58 a thermo-molecular pressure difference will be set up. In the case of liquid He II it is called the fountain effect. For simplicity we consider a one component system. It will be seen that there occurs a thermal flow as well as mass flow with interference between the two.

In order to develop the thermodynamical theory of any irreversible phenomenon it is necessary to calculate the entropy production and then find the appropriate fluxes and forces. Let the volumes of the two vessels be V. In the state of thermodynamic equilibrium the vessels will have the same energy U, the same mass M and the same entropy S. We can choose U and M as the state variables since they obey simple conservation laws. The variation $\triangle S_{\text{I}}$ of entropy of the chamber I is

$$\triangle S_{\text{I}} = \left(\frac{\partial S}{\partial U}\right)_M \triangle U + \left(\frac{\partial S}{\partial M}\right)_U \triangle M$$
$$+ \tfrac{1}{2}\left(\frac{\partial^2 S}{\partial U^2}\right)_M (\triangle U)^2 + \frac{\partial^2 S}{\partial U \partial M} \triangle U \triangle M + \tfrac{1}{2}\left(\frac{\partial^2 S}{\partial M^2}\right)_U (\triangle M)^2. \quad (23)$$

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[1] S. R. de Groot, *Thermodynamics of Irreversible Processes*, North Holland Publishing Co. (1950); I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*, Blackwell (1955); K. G. Denbigh, *Thermodynamics of the Steady State*, Methuen (1951); I. Prigogine, *Etude Thermodynamique des Phenomenes Irreversibles*, Desoer, Liege (1947).

For chamber II the variation $\triangle S$ is given by a similar expression. From conservation laws

$$(\triangle U)_{\mathrm{I}} = -(\triangle U)_{\mathrm{II}} \; ; \quad (\triangle M)_{\mathrm{I}} = -(\triangle M)_{\mathrm{II}}.$$

The total entropy variation of the entire system $2\triangle S = (\triangle S)_{\mathrm{I}} + (\triangle S)_{\mathrm{II}}$. Hence

$$\triangle S = \tfrac{1}{2}\left(\frac{\partial^2 S}{\partial U^2}\right)_M (\triangle U)^2 + \frac{\partial^2 S}{\partial U \partial M}\triangle U \triangle M + \tfrac{1}{2}\left(\frac{\partial^2 S}{\partial M^2}\right)_U (\triangle M)^2. \qquad (24)$$

Therefore the time derivative

$$\dot{\triangle} S = \dot{\triangle} U \left[\left(\frac{\partial^2 S}{\partial U^2}\right)_M \triangle U + \frac{\partial^2 S}{\partial U \partial M}\triangle M\right]$$

$$+ \dot{\triangle} M \left[\left(\frac{\partial^2 S}{\partial M^2}\right)_U \triangle M + \frac{\partial^2 S}{\partial U \partial M}\right]\triangle U \quad . \; . \; . \quad (25)$$

The energy flow

$$J_U \equiv \dot{\triangle} U \quad . \; . \; . \; . \; . \quad (26a)$$

and the mass flow

$$J_M \equiv \dot{\triangle} M. \quad . \; . \; . \; . \; . \quad (26b)$$

will be chosen as fluxes. The corresponding forces are from (5)

$$X_U \equiv \triangle\left(\frac{\partial S}{\partial U}\right)_M = \left(\frac{\partial^2 S}{\partial U^2}\right)_M \triangle U + \left(\frac{\partial^2 S}{\partial U \partial M}\right)\triangle M \; . \quad . \quad (27a)$$

$$X_M \equiv \triangle\left(\frac{\partial S}{\partial M}\right)_U = \left(\frac{\partial^2 S}{\partial M^2}\right)_U \triangle M + \left(\frac{\partial^2 S}{\partial M \partial U}\right)\triangle U \; . \quad . \quad (27b)$$

Hence (25) yields

$$\dot{\triangle} S = J_U X_U + J_M X_M \quad . \; . \; . \; . \; . \quad (28)$$

analogous to (6).

The phenomenological linear relations will then be

$$J_M = L_{11}\, X_M + L_{12}\, X_U. \quad . \; . \; . \; . \; . \quad (29a)$$

$$J_U = L_{21}\, X_M + L_{22}\, X_U. \quad . \; . \; . \; . \; . \quad (29b)$$

and

$$L_{12} = L_{21}. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (30)$$

To find out the physical consequences of (30) we must evaluate X_U amd X_M explicitly. For a simple system at constant volume we have from Problem 3(a) of p. 370,

$$TdS = dU - \mu dM. \quad . \; . \; . \; . \; . \quad (31)$$

where μ is the chemical potential per unit mass. This gives from (27a) and (27b)

$$X_U = \triangle\left(\frac{1}{T}\right) = -\frac{\triangle T}{T^2} \quad . \quad . \quad . \quad (32)$$

$$X_M = -\triangle\left(\frac{\mu}{T}\right)$$

Now $\mu = u + pv - Ts = h - Ts,$

Hence $\triangle\mu = v\triangle p - S\triangle T$

and $\triangle\left(\frac{\mu}{T}\right) = \frac{\triangle\mu}{T} - \frac{\mu}{T^2}\,\triangle T = \frac{v\triangle p}{T} - \frac{s\triangle T}{T} - \frac{\mu}{T^2}\triangle T$

Therefore $X_M = -v\,\frac{\Delta p}{T} + h\,\frac{\Delta T}{T^2}\,, \quad . \quad . \quad . \quad (33)$

Using (32) and (33) in (29a) and (29b) we get the phenomenological relations

$$J_M = -\frac{L_{11}v}{T}\,\triangle p + \frac{L_{11}h - L_{12}}{T^2}\,\triangle T \quad . \quad . \quad (34a)$$

$$J_U = -\frac{L_{21}v}{T}\,\triangle p + \frac{L_{21}h - L_{22}}{T^2}\,\triangle T \quad . \quad . \quad (34b)$$

In the stationary state $J_M=0$, and the thermo-molecular pressure difference is given by

$$\left(\frac{\triangle p}{\triangle T}\right)_{J_M=0} = (L_{11}h - L_{12})/TL_{11}v. \quad . \quad . \quad (35)$$

If on the other hand, we maintain a certain pressure difference between the two vessels and a uniform temperature throughout the system, matter flows from one vessel to the other and an associated flow of energy proportional to flow of matter is observed. The energy flow J_U can be measured by determining the heat which is necessary to maintain a uniform temperature in the system. This effect is called the thermo-mechanical effect and is given by

$$\left(\frac{J_U}{J_M}\right)_{\triangle T=0} = \frac{L_{21}}{L_{11}} = Q^*. \quad . \quad . \quad . \quad (36)$$

Hence from (35) and (30) we have

$$\left(\frac{\triangle p}{\triangle T}\right)_{J_M=0} = \frac{h-Q^*}{Tv} \quad . \quad . \quad . \quad . \quad (37)$$

which connects the two cross effects.

PHYSICAL CONSTANTS*

1 bar$=10^6$ dynes/cm$^2 = \cdot 9869$ Atm.

1 kg/cm$^2 = 0\cdot 981$ bar $= 0\cdot 97$ Atm.

The Gas Constant	R	$=(8\cdot 3166 \pm 0\cdot 0004) \times 10^7$ erg. deg.$^{-1}$ mole.$^{-1}$
Coefficient of expansion for perfect gas at 0°C		$=0\cdot 0036608$ per °C.
Ice point		$=273\cdot 16 \pm 0\cdot 01$°K.
Volume of one gram-molecule at N. T. P.		$=22\cdot 414 \pm 0\cdot 0008$ litres.
Avogadro number	N	$=(6\cdot 0247 \pm 0\cdot 0004) \times 10^{-23}$ mole^{-1}.
Number of molecules per c.c. at N. T. P.		$=(2\cdot 6870 \pm 0\cdot 0005) \times 10^{19}$ per c.c.
Mass of the H^1-atom	M	$=(1\cdot 67334 \pm 0\cdot 00010) \times 10^{-24}$ gm.
Density of mercury at N.T.P.		$=13\cdot 59504 \pm 0\cdot 00005$ gm. cm^{-3}.
Standard atmosphere		$=1\cdot 013246 \times 10^6$ dynes. cm^{-2}
Standard gravity	g	$=980\cdot 665$ cm. sec.$^{-2}$
Mechanical equivalent of heat	J	$=(4\cdot 1855 \pm 0\cdot 0004) \times 10^7$ ergs cal^{-1}
Boltzmann's constant	k	$=(1\cdot 38042 \pm \cdot 00010) \times 10^{-16}$ erg. °C^{-1}
Stefan-Boltzmann constant	σ	$=(5\cdot 6686 \pm \cdot 0005) \times 10^{-5}$ cm.$^{-2}$ deg.$^{-4}$ sec.$^{-1}$
Wien's constant	b	$=0\cdot 28979 \pm \cdot 00005$ cm. deg.
Planck's constant	h	$=(6\cdot 6252 \pm \cdot 0005) \times 10^{-27}$ erg. sec.
Velocity of light in vacuum	c	$=(2\cdot 997929 \pm \cdot 00008) \times 10^{10}$ cm. sec.$^{-1}$
Electronic charge	e	$=(4\cdot 80288 \pm 0\cdot 00021) \times 10^{-10}$ e. s. u. $=(1\cdot 60207 \pm 0\cdot 00003) \times 10^{-20}$ e. m. u.
Faraday number	F	$=96501 \pm 10$ int. coulombs per gm. equiv.
Rest mass of the electron	m	$=(9\cdot 1085 \pm 0\cdot 0006) \times 10^{-28}$ gm.
Radius of the electron	r_0	$=(2\cdot 8178 \pm \cdot 0001) \times 10^{-13}$ cm.
M_p/m_e		$=1836\cdot 13 \pm \cdot 04$
1 barn		$=10^{-24}$ cm^{-2}
Gravitation constant	G	$=(6\cdot 670 \pm 0\cdot 005) \times 10^{-8}$ dyne cm.^{2} gm.$^{-2}$

1 Mev$=1\cdot 07 \times 10^{-3}$ mass units$=1\cdot 6 \times 10^{-6}$ ergs$=4\cdot 45 \times 10^{-20}$ KWH.

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*The values given here are taken from the following sources :—Birge, *Rev. Mod. Phys.*, **13**, 233, 1941; *Phys. Rev.*, **63**, 213, 1943; *Amer. Jour. Phys.*, **13**, 63, 1945; DuMond and Cohen, *Rev. Mod. Phys.*, **25**, 691 1953. The standard error is indicated by the magnitude following ±. All quantities in this table involving the mole or the gram-equivalent. are on the chemical scale of atomic weight (O=16·0000).

SYMBOLS AND NOTATION

In case of extensive properties of a system, small italic types are used in general to denote the quantity per unit mass and capital types for the quantity per mole. In cases where confusion might arise boldface types are used to denote the quantity for an arbitrary mass or a mixture. Certain symbols have been used to denote more than one quantity so that the usual familiar symbols for each quantity can be retained but no confusion is likely to arise in the context in which they are used. Script capitals, boldface types, starred quantities and suffixed quantities have also been utilised to minimise this confusion.

English Alphabet

a any constant in general; constant in van der Waals' equation; constant in Maxwell's distribution law; accommodation coefficient; absorption coefficient; radiation constant; a_t, a_r, a_v, a_e = number of cells in phase space.

A any constant in general; first virial coefficient; area; maximum work obtainable from a system; chemical affinity; atomic weight; electron affinity.

b any constant; constant in van der Waals' equation; constant in Maxwell's distribution law; breadth or half-width; Wien's constant; b_i = coefficient of internal pressure.

B any constant; second virial coefficient; $B=h/8\pi^2I$; Faraday number.

c any constant; proportional concentration; mean temperature coefficient of resistance; specific heat (c_p, c_V, c_s); velocity of light; velocity of elastic wave (c_l, c_t); restoring couple per unit twist; molecular velocity (c, resultant; $\bar{c}$, mean).

C a constant; molar specific heat; third virial coefficient; root mean square velocity.

d diameter; density; thickness; lattice spacing; symbol for differentiation.

D Diffusion coefficient; heat of dissociation; D_T = thermal diffusion coefficient.

e emissive power; electronic charge; base of Naperian logarithm.

E	e.m.f.; elasticity (E_T, isothermal; E_s, adiabatic); energy (E_t, E_r, E_e, $E(r)$); emissive power of blackbody; electrical field (E_x, E_y, E_z).
f	free energy; any function; partition function; fraction of molecules absorbed.
F	force; any function; partition function (F_r, F_t, F_e); free energy; $F^* =$ decrease in free energy.
g	gravity; Gibbs function; volume of elementary cell; a priori probability of cell; statistical weight; Lande factor.
G	Gibbs function; phase volume.
h	height; quantity of heat; enthalpy; Planck's constant; diffusivity; Millerian index.
H	height; quantity of heat; enthalpy; Boltzmann H-function; Hamiltonian; $\mathscr{H} =$ magnetic field.
i	$\sqrt{-1}$; electric current; chemical constant; nuclear spin.
I	moment of inertia; intensity of radiation; integration constant of reaction isobar; $\mathscr{I} =$ intensity of magnetisation.
j	inner quantum number.
J	mechanical equivalent of heat; flux.
k	a constant; Boltzmann's constant; bulk modulus; wave vector (k, k_x, k_y, k_z); Millerian index; k_T, = thermal diffusion ratio.
K	a constant; thermal conductivity; specific intensity of radiation; K_p, K_x, K_ν, equilibrium constant of chemical reaction; $\mathscr{K} =$ dielectric constant.
l	length; latent heat per unit increase of volume; direction cosine; Millerian index.
L	length; latent heat; kinetic energy; self-inductance.
m	mass of molecule; mass in general; direction cosine; $n \equiv \sqrt{\mu/h}$; magnetic quantum number.
M	mass of a gram-molecule; molecular weight; mass in general; thermal capacity; Mach number; $\mathscr{M} =$ magnetisation per mole; $\bar{M} =$ mean molecular weight; $M^* =$ mass flowing
n	any number; number of molecules per c.c.; frequency of sound; modulus of rigidity; constants in force law; n^*, number of moles.

N	any number; Avogadro number; total number of molecules in the vessel.
p	pressure; generalised momentum; number of cells; perimeter; p^*= pressure ratio.
P	thermodynamic probability; collision rate.
q	quantity of heat; generalised coordinate; dryness factor.
Q	quantity of heat; heat of reaction (Q_p, Q_V.)
r	radius; ratio; reflection coefficient.
R	gas constant per mole; electrical resistance; radius; R^* = reheat factor.
s	specific heat; distance; entropy; rotational quantum number.
S	entropy; solar constant.
t	temperature in °C; time; transmission coefficient.
T	temperature in °K; periodic time ; T_0, volume of gas flowing out per unit pressure difference; $\mathcal{T}$ = surface tension.
u	internal energy; energy density of radiation; molecular velocity; u_0=velocity of flow of gas.
U	internal energy; molecular velocity relative to layer; U_i = energy of ionization of one gram-atom; U_r = heat of reaction; U^*=decrease in internal energy.
v	any volume; volume of one gram of gas; molecular velocity; vibrational quantum number; v_0=velocity of flow of gas.
V	any volume; volume of one mole of gas; potential energy; molecular velocity relative to layer; $\mathcal{V}$= velocity of wave, velocity of sound; V_i=ionization potential; V_0 = volume of gas flowing.
w	molecular velocity; any velocity; mass.
W	thermal capacity of calorimeter; work done; mathematical probability; W_r, resistance of tube to flow of gas.
x	variable distance; a variable quantity; concentration.
X	a variable term; force; electrical field.
y	coordinate of position.
Y	component of force; $\mathcal{Y}$ = Young's modulus.
z	coordinate of position.
Z	component of force.

Greek Alphabet

Alpha	α	any constant; constant of platinum thermometer; coefficient of volume expansion of gas; α-rays; some angle; most probable velocity; polarizability of a molecule; deviation from equilibrium value; thermal diffusion factor; $\alpha = -\ln f$.
Beta	β	any constant; constant of platinum thermometer; coefficient of pressure expansion; β-rays; some angle; volume of sphere of influence; coefficient of performance; modulus of distribution.
Gamma	γ	any constant; ratio of specific heats; coefficient of expansion of vessel; γ-rays; volume of $6N$-dimensional phase space.
,,	Γ	gamma for mixture; number of molecules crossing.
Delta	δ	small change; constant of platinum thermometer.
,,	Δ	small change; Brownian displacement.
Epsilon	ϵ	any constant; small quantity; energy; coefficient of external friction.
Zeta	ζ	coefficient of slip.
Eta	η	viscosity; efficiency; Joule coefficient $(\partial T/\partial p)_u$.
Theta	θ	temperature °C; angle.
,,	Θ	excess of temperature; characteristic temperature.
Iota	ι	
,,	ϑ	saddle point in complex integration.
Kappa	κ	compressibility.
Lambda	λ	a constant; wave-length; mean free path; coefficient of linear expansion; number of moles of gas; molar latent heat; λ-point; direction cosine; standard deviation; coordinate of position.
Mu	μ	momentum; force per unit displacement; torsional couple per unit twist; force parameter; volume in molecular phase space; dipole moment; Joule-Thomson coefficient; refractive index; molecular weight; direction cosine; micron $(=10^{-3}$ mm.); micro- (10^{-6}); Bohr magneton; $\mu = Ep/\rho Ac$; μ_p=protonic magnetic moment; μ_i = chemical potential of i-th, specie.
Nu	ν	number of collisions; number of moles per unit volume; number of molecules crossing; frequency, stoichiometric coefficient.
Xi	ξ	momentoid; displacement; $\xi = h\nu/kT$.
Omicron	o	

Pi	π	Poltier coefficient; ratio of circumference to diameter.
,,	Π	symbol for product.
Rho	ρ	density.
Sigma	σ	molecular diameter; specific heat of water; Thomson coefficient; electrical conductivity; Stefan's constant; $\sigma = \Theta/T$.
,,	Σ	symbol for summation.
Tau	τ	interval of time; temperature; element of phase volume.
Upsilon	υ	
Phi	ϕ	excess of temperature; displacement in vibrating medium.
,,	Φ	
Chi	χ	magnetic susceptibility; ionisation (χ_s) and excitation ($\chi_{r,s}$) energy of atom.
Psi	ψ	any function : Planck's function; thermal resistance; Schrödinger wave function.
,,	Ψ	Schrödiner wave function
Omega	ω	angular velocity; fractional number; wave number.
,,	Ω	solid angle

Mathematical symbols

∂	symbol for partial differentiation
d	,, ,, total differentiation
$\sim$	of the order of
$\cong$	approximately equal to
$\equiv$	equal by definition
$\propto$	is proportional to
∇^2	Laplacian operator

Abbreviations

A	Angström
esu	electrostatic unit
emu	electromagnetic unit
emf	electromotive force
ev	electron volts
kev	kiloelectron volts
Mev	million electron volts
gm	gram
amp	amperes
cm	centimetre
mm	millimetre

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